

**TRANSMITTAL OF APPEAL BRIEF  
(Large Entity)**

Docket No.  
71024-023

In Re Application of: Warran B. Lineton

Serial No.  
10/643,097

Filing Date  
August 18, 2003

Examiner  
David Thomas Beck

Group Art Unit  
1732

Title: METHOD OF FABRICATING PTFE MATERIAL

**TO THE COMMISSIONER FOR PATENTS:**

Transmitted herewith is the Appeal Brief in this application, with respect to the Notice of Appeal filed on:  
September 1, 2005

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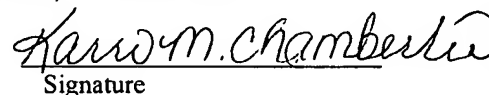
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

APPLICANT: Warran B. Lineton  
SERIAL NO: 10/643,097  
FILED: August 18, 2003  
FOR: METHOD OF FABRICATING PTFE MATERIAL  
EXAMINER: David Thomas Beck

Board of Patent Appeals and Interferences  
United States Patent and Trademark Office  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

December 1, 2005

Sir:

**APPEAL BRIEF**

This brief is submitted in support of the Notice of Appeal of the Final Rejection filed September 1, 2005.

**(I) REAL PARTY IN INTEREST**

This application is assigned to Federal-Mogul Worldwide, Inc which is wholly owned by Federal-Mogul Corporation.

**(II) RELATED APPEALS AND INTERFERENCES**

There are no other appeals or interferences known to appellant, the appellant's legal representative, or the assignee which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal

**(III) STATUS OF CLAIMS**

All claims 1-9 are on appeal.


**(IV) STATUS OF AMENDMENTS**

An after-final response was filed on August 5, 2005 and was acted upon by the

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**CERTIFICATE OF MAILING**

I hereby certify that this Brief for U.S. Serial No.: 10/643,097 filed August 18, 2003 is being deposited with the United States Postal Service as Express Mail Label No. EV377751857US, in an envelope addressed to Board of Patent Appeals and Interferences, United States Patent and Trademark Office, Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450 on December 1, 2005.

  
Karri M. Chamberlin

examiner in an advisory action dated August 24, 2005. The after-final response and the examiner's advisory action set forth the opposing views with respect to the merits of the final rejection at issue in this appeal.

#### **(V) SUMMARY OF CLAIMED SUBJECT MATTER**

This invention relates to a method of fabricating polytetrafluorethylene (PTFE) material. There are two independent claims drawn to the inventive method, namely claims 1 and 8.

Claim 1 calls for a mixture of PTFE resin powder and a susceptor material to be prepared. The mixture is fed into a compaction zone to at least partially compact and shape the mixture. A continuous flow of the mixture is fed from the compaction zone to a heating zone where the mixture is heated and sintered by exciting the susceptor material by application of wave energy.

Independent claim 8 calls for the preparation of a mixture of PTFE resin powder and a susceptor material. The mixture is compacted and then sintered by exciting the susceptor material with microwave energy.

Referring to the Figures and specification, the mixture is generally indicated at 12, the compaction zone at 14 and the heating zone at 24.

#### **(VI) GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL**

1. Whether claims 1 and 5-8 are unpatentable over Adams et. al. in view of Hori et. al.
2. Whether claims 2-4 and 9 are unpatentable over Adams et. al. in view of Hori et. al. and Eucker et. al.

#### **(VII) ARGUMENT**

It is the appellant's position that the examiner has failed to establish a proper prima facie rejection of the appealed claims and that the rejections should be reversed by this Board.

##### **Claims 1 and 5-8**

Claim 1, as summarized above in Section V, calls for the PTFE resin powder to be mixed with a susceptor material and then fed into a compaction zone to at least partially compact and shape the mixture after which the mixture is fed continuously from the compaction zone to a heating zone where the mixture is heated and sintered by exciting the susceptor material through application of wave energy. Claim 8 calls for the wave energy to be microwaves.

The examiner cites as the primary reference Adams et al (Appendix B). The examiner concedes that Adams et al fails to disclose the recited step of preparing a mixture of PTFE resin and a susceptor material. It was pointed out to the examiner in response to the initial rejection and in the after-final reply that Adams et al further teaches against incorporating a volatile additive (i.e., one which is driven off by heat to impart porosity to the centered product). See column 2, line 60 through column 3, line 8. It was further pointed out that Adams et al does not invite a broad range of materials to be incorporated into the process, but ones possessing a sufficiently high “loss factor” to be effectively heated with dielectric heat. The usable range is set at about 0.08 to about 0.2. See column 4, lines 22-25. It was demonstrated to the examiner that PTFE has a dielectric loss factor of about 0.0002. More than two orders of magnitude below the 0.08 limit.

Nowhere does Adams et al invite or suggest usage of PTFE material as the base starting material and it is respectfully submitted that based on the stated criteria, one skilled in the art would not consider using PTFE in the process of Adams et al due to its extremely low loss factor. Instead, Adams et al carefully selects the material based on its dielectric properties which are favorable to dielectric heating, and teaches that a particular combination of particle sizes as taught at column 7, lines 23-27 and 54-64, in combination with an amount of water, as disclosed at column 7, line 62 through column 8, line 2 to achieve the best results with dielectric heating.

The examiner appears to be disregarding these express teachings of the primary reference and looking to Hori et al in order to substitute its material for that set forth in Adams et al. As explained in detail below, the examiner further suggests modifying the material of Hori et al so as to pick and choose among only those constituents of the mixture that support the rejection and to disregard the rest as not being needed. It is respectfully submitted that the examiner is failing to take into account all of the teachings of the cited prior art, including that which would direct one skilled in the art away from making the combination called for by the examiner. While Hori et al does in fact start out with PTFE and does incorporate carbon into the PTFE mixture, it also requires that the mixture be combined with an extrusion lubricant in order to meet the objectives set forth in Hori, which is to produce, ultimately, a wide width ribbon of the PTFE material that is highly conductive in the longitudinal direction and nearly uniform in cross section for use in battery terminals and fuel cell applications. In other words, the PTFE base material, which is inherently non-

conductive, has conductive powder carbon added and a process is set forth by Hori by which extremely wide width, longitudinally conductive and cross-sectionally uniform ribbons of the material can be prepared. Hori sets forth in the background prior production limitations which were unable to produce a ribbon width greater than 160mm while maintaining the longitudinal conductivity and cross-sectional consistency. There is no teaching or suggestion in Hori or in Adams, for that matter, of utilizing the carbon powder in a PTFE compound as a susceptor material for purposes of heating and sintering the material in the presence of wave energy, but rather to produce conductivity in the end product. The process described in connection with the material of Hori involves mixing the PTFE and carbon powder with an extrusion lubricant ranging in amount between 10 to 60 percent by weight of the PTFE and carbon powder material. The examiner has chosen to disregard the need for the extrusion lubricant for reasons that “Adams et al does not require an extrusion lubricant”, but this ignores the fact that the secondary Hori reference requires it to be present in connection with processing the PTFE material. The rejection further improperly bypasses the restriction in Adams that the materials not contain any volatile additives. Hori expressly teaches at column 5, lines 26-29 that the extruded, non-sintered PTFE material is first heated to between 100-260°C “to remove the extrusion lubricant”. In other words, the extrusion lubricants are intentionally selected by Hori as ones that are volatile so that they can be driven off by the application of heat prior to sintering. Adams et al forbids such volatile compounds. The examiner cannot simply ignore these teachings against using the Hori material in the process of Adams and cannot simply modify the material of Hori to exclude the extrusion lubricants since it is clearly called for and required by Hori.

Lacking proper support in the prior art to make the combination, it is apparent that the basis for modifying the references is improper hindsight reconstruction of applicant’s own invention, and it is neither proper nor obvious to reject a claim based on hindsight. It is respectfully requested, therefore, that this Board reverse the decision of the examiner with respect to claims 1 and 5-8.

#### Claim 2

The examiner concedes that Adams et al in view of Hori et al fails to teach the step of drawing a vacuum on the mixture within the heating zone to extract air from the mixture. However, the examiner proposed to modify Adams and Hori by the teachings of Eucker. The examiner fails to consider what effect the vacuum would have on the ability of the process of

Adams to produce a material that is porous. It would seem that the vacuum would cause the voids in the material to collapse or at least have a negative effect on developing porosity. If so, it would seem reasonable that one skilled in the art would be lead away from using a vacuum. The motivation given by the examiner for drawing the vacuum is “to remove volatiles from inside the tube”. However, Adams prohibits the presence of volatiles in the in starting material (see column 2, line 60 to column 3, line 8). As such, the stated motivation does not exist in the cited art and thus the rejection is defective. It is respectfully requested that this Board reverse the decision of the examiner with respect to claim 2.

**(VIII) CLAIMS APPENDIX**

See Attachment A.

**(IX) EVIDENCE APPENDIX**

None.

**(X) RELATED PROCEEDINGS APPENDIX**

None.

**(XI) CITED REFERENCES APPENDIX**

Claims (attachment A)

Adams (attachment B)

Hori (attachment C)

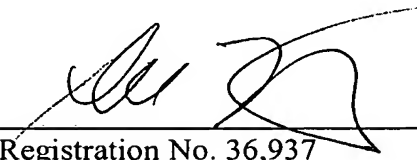
Eucker (attachment D)

It is believed that all claims on appeal clearly are allowable over the prior art of record. Accordingly, reversal of the final rejection and the allowance of all claims on appeal are requested.

Respectfully submitted,

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1. A method of fabricating PTFE material comprising:  
preparing a mixture of PTFE resin powder and a susceptor material;  
feeding the mixture into a compaction zone to at least partially compact and shape the mixture; and  
providing a continuous flow of the mixture from the compaction zone to a heating zone and heating and sintering the mixture within the heating zone by exciting the susceptor material by application of wave energy.
2. The method of claim 1 including drawing a vacuum on the mixture within the heating zone to extract air from the mixture.
3. The method of claim 2 wherein the heating zone has an initial stage for preheating and finishing compaction of the mixture prior to sintering the mixture.
4. The method of claim 2 including passing the sintered mixture through a cooling zone following the heating zone.
5. The method of claim 1 including cutting the PTFE material while the mixture is at a temperature below a sintering temperature within the heating zone but above ambient temperature.
6. The method of claim 1 wherein the mixture is compacted into a generally tubular form.
7. The method of claim 1 wherein the mixture is heated by microwave energy.
8. A method of fabricating a PTFE material, comprising:  
preparing a mixture of PTFE resin powder and a susceptor material;  
compacting the mixture; and  
sintering the mixture by exciting the susceptor material with microwave energy.
9. The method of claim 8 including drawing a vacuum on the mixture during the sintering step to extract air from the mixture.

[54] **METHOD FOR PRODUCING SINTERED POROUS POLYMERIC ARTICLES**

[75] Inventors: Richard C. Adams, Chardon; Albert J. Herold, Bedford, both of Ohio

[73] Assignee: The Standard Oil Company, Cleveland, Ohio

[21] Appl. No.: 217,886

[22] Filed: Dec. 18, 1980

[51] Int. Cl.<sup>3</sup> ..... H05B 1/00

[52] U.S. Cl. .... 264/25; 264/26; 264/126; 264/141; 264/143

[58] Field of Search ..... 264/25, 26, 126, 141, 264/143

[56] **References Cited**

**U.S. PATENT DOCUMENTS**

1,742,515	1/1930	Mandell	264/43
1,873,223	8/1932	Sherwood	75/212
1,934,383	11/1933	Stafford	501/85
2,085,047	6/1937	Schneider	106/122
2,252,277	8/1941	Tate et al.	252/503
2,356,076	8/1944	Moberly	252/506
2,400,091	5/1946	Alfthan	264/115
2,413,498	12/1946	Hill	264/127
2,456,262	12/1948	Fields	264/120

2,710,991	6/1955	Parkhurst	264/113
2,862,278	12/1958	Engel et al.	264/141
2,985,918	5/1961	Moore et al.	264/53
3,058,166	10/1962	Fields	264/54
3,426,102	2/1969	Selak et al.	525/310
3,519,517	7/1970	Dench	264/26
3,586,737	6/1971	Duke et al.	525/310
3,646,188	2/1972	Campbell	264/25
4,000,106	12/1976	Isley	260/31.8 DR
4,041,005	8/1977	Talsma et al.	260/32.8 A
4,151,151	4/1979	Isley	252/434
4,216,179	8/1980	Lamberts et al.	264/25
4,268,465	5/1981	Suh et al.	264/25

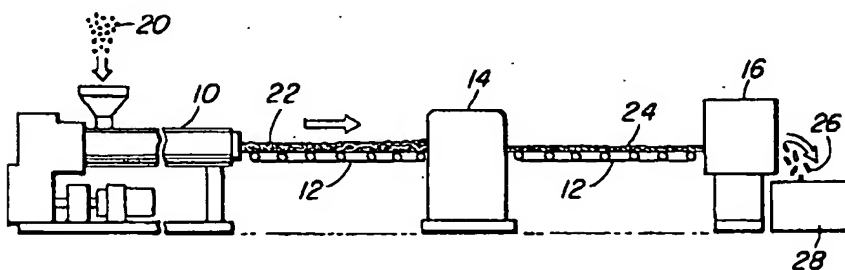
*Primary Examiner*—James R. Hall

*Attorney, Agent, or Firm*—William D. Mooney; Herbert D. Knudsen; Larry W. Evans

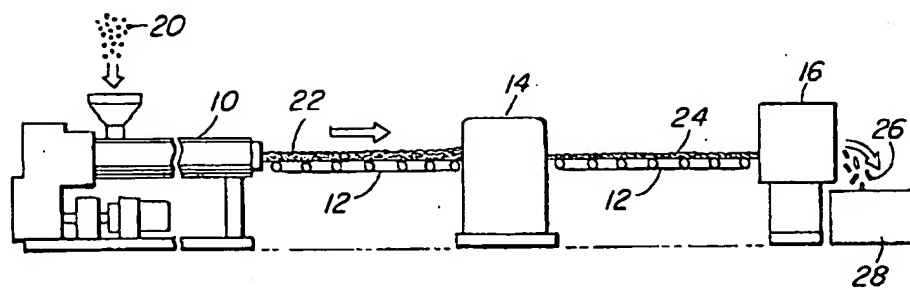
[57] **ABSTRACT**

A process for forming sintered porous polymeric articles by the steps of sintering preforms of polymeric particles with dielectric heat, or with dielectric heat in combination with conventional heating techniques. Sintered porous polymeric articles made of rubber-modified nitrile resins in accordance with the foregoing processes are also disclosed.

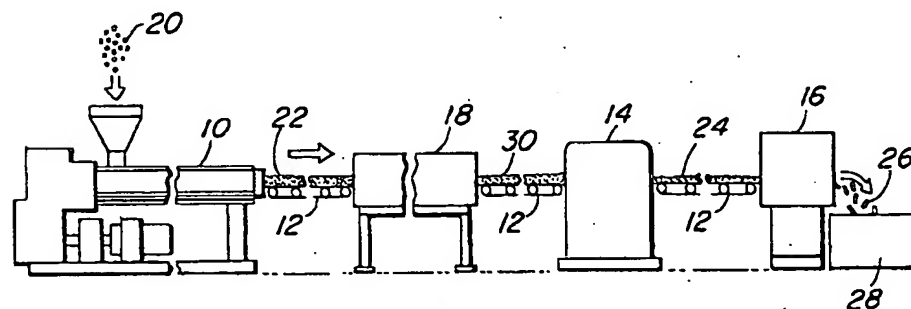
38 Claims, 3 Drawing Figures



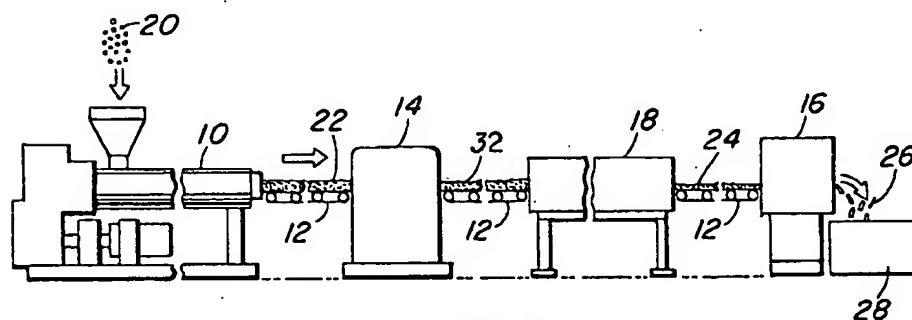




**Fig. 1**



**Fig. 2**



**Fig. 3**

# METHOD FOR PRODUCING SINTERED POROUS POLYMERIC ARTICLES

## TECHNICAL FIELD

This invention relates to a method of forming sintered porous polymeric articles, and the articles produced therefrom. More particularly, this invention relates to a method of sintering a preform of discrete polymeric particles using dielectric heat alone or in combination with conventional heat.

## BACKGROUND OF THE INVENTION

Sintering is the welding together of small particles by heating such particles without melting them at temperatures below the temperature at which they flow completely; the particles are fused together to form a relatively strong mass, but the mass as a whole does not melt. Sintering is used in powder metallurgy but has application with ceramics, cellulose derivatives and polytetrafluoroethylene resin compositions. The prior art methods for producing sintered articles generally comprises the steps of introducing finely divided powder into a mold, compressing the powder to a preform of a desired shape, heating the preform at a sintering temperature, and then cooling the sintered article. When sintered articles with porous structures are desired, volatile materials are generally mixed with the preform; upon sintering the volatile material evaporates or escapes leaving voids in the sintered product.

Examples of these methods are disclosed in U.S. Pat. Nos. 1,873,223 (sintering a mixture of metal particles and a volatile lubricant to form porous bearings or similar articles), 1,742,515 and 1,934,383 (sintering ceramic particles in the presence of a volatile component to form porous bricks), 2,085,047 (forming a porous article by heating a mixture of a derivative of cellulose and a salt or other compound that is insoluble in the mixture at a temperature high enough to decompose the salt or other compound but not high enough to melt the cellulose derivative), 2,252,277 (heating a mixture of "Bakelite" and a pore forming substance at a high enough temperature to evacuate the latter leaving a porous structure), and 2,356,076 (forming a porous carbon plate by heating a mixture of green carbon fluor and particles of a volatile substance at a temperature that causes the latter to change to a gas and escape leaving cavities conforming to the original particles).

U.S. Nos. 2,400,091; 2,413,498; 2,456,262; 2,710,991; and 2,985,918 disclose various techniques for shaping sintered articles of polytetrafluoroethylene. U.S. Pat. No. 2,400,091 discloses a process for producing a porous article by the steps of heating polytetrafluoroethylene at a temperature in the range of 327° C. to 500° C., cooling the polymer to a temperature below 327° C., subdividing the cooled polymer to a particle size less than about 20 mesh, forming the finely divided polymer in the shape of the desired article by pressing it in a mold at a temperature below 327° C., heating the shaped polymer at a temperature between 327° C. and 500° C. until it is heated throughout to said temperature, and cooling the resulting article. U.S. Pat. No. 2,413,498 discloses a molding process that includes the steps of mixing polytetrafluoroethylene and a heat-decomposable film-forming material and then removing the film-forming material at a temperature sufficiently high to flash off the film-forming material, and continuing heating until the polytetrafluoroethylene coalesces in the

form of desired shaped articles such as rods, tubes, and unsupported forms. U.S. Pat. No. 2,456,262 discloses a process of fabricating polytetrafluoroethylene articles by the steps of subjecting finely divided polytetrafluoroethylene to a pressure in a die to form a shaped body, releasing the pressure and removing the shaped body from the die, heating the shaped body at a temperature above 327° C. until it is sintered, and cooling the shaped body to a temperature below 250° C. under pressure in a die having the shape of the desired finished article. U.S. Pat. No. 2,710,991 discloses a method of producing thin sheet-like articles from polytetrafluoroethylene which includes the steps of molding preforms at substantially room temperature, releasing the molding pressure, heating the preforms to a sintering temperature and then cooling the sintered article. The preforms are molded from the polymer in dry powdered form by spreading a plurality of charges of the dry powder one above the other in the mold, the charges being separated by flexible separator sheets, and consolidating the charges by the application of pressure. U.S. Pat. No. 2,985,918 discloses a process for forming shaped lengths of polytetrafluoroethylene having a cellular structure that includes the steps of extruding through a die a paste composition of finely divided polytetrafluoroethylene and finely divided methyl methacrylate polymer intimately mixed with a volatile organic lubricant and thereafter heating the resultant shaped article to sinter the polytetrafluoroethylene and to decompose and volatilize the acrylic polymer to form minute interconnecting pores throughout the article.

The prior art methods teach the use of conventional heating techniques. The term "conventional heating", and cognate terms such as "conventional heat", are used herein to mean heating by conduction or convection or a combination thereof using a conventional heating source, such as an open flame or a heating coil, with the heat being transferred to the article being heated by a solid, liquid or gaseous (e.g., air) medium. Conventional heating is not used herein to include "dielectric heating" which is defined hereafter.

Effective sintering of polymeric preforms to attain desirable levels of strength and porosity for the sintered articles produced therefrom requires sufficient fusing of the individual polymeric particles both at the surface and in the interior of the article without such particles completely melting. Porous polymeric preforms exhibit relatively poor heat transfer characteristics (partially due to their porous structure) and, consequently, effective sintering of such materials can be attained with conventional heating only at the cost of lengthy and carefully monitored heating cycles. Insufficient heating results in sintered articles with poor fusion in their interiors and, consequently, inadequate strength. Overheating results in sintered articles with overfusion on their exterior surfaces and, consequently, inadequate porosity. The proposal of admixing volatile components to compensate for the lengthy carefully monitored heating cycles results in additional preform preparation procedures and, in some instances, procedures for removing excess volatiles subsequent to sintering. Additionally, careful monitoring and control of the heating cycle is still required to avoid cracking or splitting due to excessively rapid or uncontrolled evaporation of the volatile component.

## SUMMARY OF THE INVENTION

It has now been discovered that sintered porous polymeric articles with good strength and porosity characteristics can be formed with relatively short and easy to control heating cycles and without the necessity of admixing volatile components by a method comprising heating preforms of the articles with dielectric heat. The term "dielectric heat", and cognate terms such as "dielectric heating", are used herein to mean heating by the penetration of electromagnetic radiation in the range of about 1 to about 10,000 MHz. Dielectric heating encompasses both high-frequency heating and microwave heating. High-frequency heating, which is sometimes referred to as radio-frequency heating, utilizes frequencies in the range of about 1 to about 200 MHz. Microwave heating utilizes frequencies above about 890 MHz, and preferably in the range of about 890 MHz to about 10,000 MHz. Broadly stated, the invention contemplates a method for producing a sintered porous polymeric article comprising heating a preform of polymeric particles with dielectric heat. In a preferred embodiment, the invention contemplates sintering a preform of polymeric particles with a combination of dielectric heat and conventional heat.

Further, the invention contemplates a continuous process and the apparatus therefor for forming sintered porous polymeric articles comprising forming a preform of polymeric particles and sintering the preform with dielectric heat alone or with a combination of dielectric heat and conventional heat. In a preferred embodiment, the invention contemplates forming a continuous length of packed polymeric particles comprising the preform. In a particularly advantageous embodiment, the preform is formed by extruding the polymeric particles.

Further, the invention contemplates a compressed mass of polymeric particles suitable for sintering with dielectric heat. In a preferred embodiment the invention contemplates a preform comprising a mixture of coarse polymeric particles and fines. In still another preferred embodiment the invention contemplates a preform comprising a compressed mass of polymeric particles and an effective amount of water to enhance the strength of the sintered article formed therefrom.

The product of this process comprises a porous sintered polymeric article. In a particularly advantageous and, therefore, greatly preferred embodiment, the product of the present invention comprises a rubber-modified nitrile resin. Sintered articles made in accordance with the present invention from such rubber-modified nitrile resins are advantageously chemically resistant and hydrophilic in character.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partially fragmented elevational view of apparatus used in accordance with the present invention for forming sintered porous polymeric articles by the steps of extruding a preform of a continuous length of packed polymeric particles and sintering the preform in a dielectric heat oven;

FIG. 2 is a partially fragmented elevational view of apparatus used in accordance with the present invention for forming sintered porous polymeric articles by the steps of extruding a preform of a continuous length of packed polymeric particles, heating the preform with conventional heating techniques, and, subsequently, sintering the preform with dielectric heat; and

FIG. 3 is a partially fragmented elevational view of apparatus used in accordance with the present invention for forming porous polymeric articles by the steps of extruding a preform comprising a continuous length of packed polymeric particles, followed by the steps of heating the preform with dielectric heat and then completing the sintering process with conventional heating techniques.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

Further features and advantages of the invention will be apparent from the detailed description of the preferred embodiment herein set forth.

The present invention will be described hereinafter as applied particularly to rubber-modified nitrile resins. It is to be understood, however, that the starting material of the process of the invention (i.e., the polymeric materials to be sintered) may be any polymeric material or polymeric composition with a sufficiently high "loss factor" (hereinafter defined) to be effectively heated with dielectric heat. In preferred embodiments the starting materials are selected from polymers or polymer compositions having loss factors above about 0.08, preferably above about 0.2.

The term "loss factor" is used herein to mean the product of the "power factor" and the "dielectric constant" of a material. In the case of a perfect, or lossless, dielectric, the displacement current leads the voltage by a temporal phase angle of 90°. For an imperfect dielectric the phase angle is less than 90°. The cosine of the phase angle is the "power factor". Between any two electrically charged bodies there is a force (attraction or repulsion) which varies according to the strength of the charges, the distance between the bodies, and a characteristic of the medium separating the bodies (the dielectric) known as the "dielectric constant". This force,  $f$ , is found by the equation

$$f = \frac{q_1 q_2}{\epsilon r^2}$$

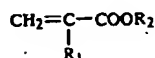
in which  $q_1$  and  $q_2$  are the respective charges,  $r$  is the distance, and  $\epsilon$  is the dielectric constant. For a vacuum  $\epsilon$  is 1.0000; for air,  $\epsilon = 1.00059$ . In practice the dielectric constant of a material is found by measuring the capacitance of a parallel plate condenser using the material as the dielectric, then measuring the capacitance of the same condenser with a vacuum as the dielectric, and expressing the result as a ratio between the two capacitances. Further discussions concerning dielectric heating, high frequency and microwave equipment selection and design, and a partial listing of loss factors for various polymers or polymeric compositions can be found in "Encyclopedia of Polymer Science and Technology", Interscience Publishers, a division of John Wiley & Sons, Inc., Volume 5, pages 1 to 23, which is incorporated herein by reference.

The rubber-modified nitrile resins embodied herein are those which result from the polymerization of a major portion of an olefinically unsaturated nitrile, optionally another monomer component, and in the presence of a preformed rubber component by methods known to those skilled in the art.

The polymers which are most useful in the process of this invention include those produced by polymerizing a major proportion of a monounsaturated nitrile, such as

acrylonitrile, and optionally a minor proportion of another monovinyl monomer component copolymerizable with said nitrile in an aqueous medium in the presence of a preformed diene rubber which may be a homopolymer or a copolymer of a conjugated diene monomer.

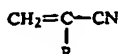
The esters of olefinically unsaturated carboxylic acids include those having the structure



wherein  $\text{R}_1$  is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or a halogen, and  $\text{R}_2$  is an alkyl group having from 1 to 6 carbon atoms. Compounds of this type include methyl acrylate, ethyl acrylate, the propyl acrylates, the butyl acrylates, the amyl acrylates, and the hexyl acrylates; methyl methacrylate, ethyl methacrylate, the propyl methacrylates, the butyl methacrylates, the amyl methacrylates, and the hexyl methacrylates; methyl alpha-chloroacrylate, ethyl alpha-chloroacrylate, and the like. Most preferred in the present invention are methyl acrylate, ethyl acrylate, methyl methacrylate, and ethyl methacrylate.

The conjugated diene monomers useful in the present invention include butadiene-1,3, isoprene, chloroprene, bromoprene, cyanoprene, 2,3-dimethyl-butadiene-1,3, 2-ethyl-butadiene-1,3, 2,3-diethyl-butadiene-1,3, and the like, and others. Most preferred for the purpose of this invention are butadiene-1,3 and isoprene because of their ready availability and their excellent copolymerization properties.

The olefinically unsaturated nitriles useful in the present invention are the alpha, beta-olefinically unsaturated mononitriles having the structure

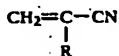


wherein R is hydrogen, a lower alkyl group having from 1 to 4 carbon atoms, or a halogen. Such compounds include acrylonitrile, alpha-chloroacrylonitrile, alpha-fluoroacrylonitrile, methacrylonitrile, ethacrylonitrile, and the like. The most preferred olefinically unsaturated nitriles in the present invention are acrylonitrile and methacrylonitrile and mixtures thereof.

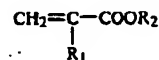
The other monovinyl monomer component copolymerizable with the olefinically unsaturated nitriles which is useful in this invention includes one or more of the esters of olefinically unsaturated carboxylic acids.

Polymerizates of particular utility in this invention and details of their method of preparation are described in U.S. Pat. Nos. 3,426,102; 3,586,737; 4,000,106; 4,041,005; and 4,151,151, these references being incorporated herein by reference.

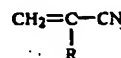
Specific polymerizates useful in the process of this invention include those prepared by the polymerization of 100 parts by weight of (A) at least 50% by weight of at least one nitrile having the structure



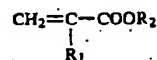
wherein R has the foregoing designation and (B) up to 50% by weight based on the combined weights of (A) and (B) of an ester having the structure



wherein  $\text{R}_1$  and  $\text{R}_2$  have the foregoing respective designations, in the presence of from 1 to 40 parts by weight of (C) a rubbery polymer of a conjugated diene monomer selected from the group consisting of butadiene and isoprene and optionally a comonomer selected from the group consisting of styrene, a nitrile monomer having the structure



wherein R has the foregoing designation, and a monomer having the structure



wherein  $\text{R}_1$  and  $\text{R}_2$  have the foregoing respective designations, said rubbery polymer containing from about 50 to 100% by weight of polymerized conjugated diene and from about 0 to 50% by weight of comonomer.

Preferably, component (A) should be present in from about 60 to 90% by weight based on the combined weights of (A) and (B) and the rubbery polymer (C) should contain more than 50% by weight of conjugated diene and more preferably from 60 to 90% by weight of the conjugated diene. Materials within this class are commercially available from the Standard Oil Company (Ohio), Cleveland, Ohio, under the trade name "Barex".

The polymerizates useful in the process of this invention can contain compounding ingredients and additives, pigments, colorants, stabilizers, etc., as is well known in the art, so long as the balance between impact strength, flexural strength, tensile strength, processability, heat-distortion temperature, and the like, is not affected to such a degree that the article is no longer useful for its intended purpose.

Subdivision of the starting material into discrete polymeric particles can be accomplished by a variety of mechanical methods such as with a hammer mill, a stamping mill, an attrition mill, a rotary cutter or a Wiley mill. Such methods are entirely conventional in procedure and equipment, structure and operation, and, being well known to those skilled in the art, need not further be described. The starting material is reduced until substantially all of it passes through a No. 16 Tyler mesh sieve and, preferably, a No. 70 Tyler mesh sieve.

As a particular feature of the invention preforms of compressed shaped masses of the subdivided starting material are formed prior to sintering. The subdivided starting material is shaped to the form of the desired sintered article by, for example, compacting the subdivided particles of starting material in a mold at a temperature below the melting point of the material, preferably at room temperature. In preferred embodiments of the invention subdivided particles of rubber-modified

nitrile resin compositions are compacted at temperatures below about 120° C., preferably at room temperature. Pressures of from about 100 to about 4000 pounds per square inch (PSI) are preferably employed in shaping the preforms in the mold. In some instances, however, particularly when temperatures above room temperature are employed, the preforms are formed with no applied pressure or with pressures below about 100 PSI. Alternatively, depending on the shape, size and porosity of the desired preform and the sintered article to be made therefrom, higher pressures, up to 10,000 PSI or more, are used.

The preform can be sintered in the mold or removed from the mold prior to sintering. If the preform is sintered in the mold, sintering can be conducted with pressures as above described applied to the preform, the amount of pressure, if any, being dependent upon the desired strength and porosity of the article to be sintered. If the preform is sintered in the mold, non-metallic molds (e.g., ceramic, plastic, etc.) must be used to avoid deleterious effects of dielectric heating.

In a particularly advantageous embodiment of the invention an effective amount of particle fines of starting material are mixed with the subdivided starting material prior to forming the preform to enhance the strength of the sintered article produced therefrom. The fines are formed during the subdivision process discussed above and comprise particles of starting material small enough to pass through a No. 240 Tyler mesh sieve. The fines are mixed with the subdivided starting materials at a ratio of up to about 100%, preferably about 5% to about 25%, by weight based on the combined weight of particles in the preform. Accordingly, in this embodiment, the preform comprises from about 0% to about 100%, preferably about 75% to about 95%, by weight based on the total weight of the preform of coarse particles of starting material. The term "coarse particles" as used in the specification and claims means particles small enough to pass through a No. 16 Tyler mesh sieve, preferably a No. 70 Tyler mesh sieve, but large enough to be retained on a No. 240 Tyler mesh sieve.

In a preferred aspect of the invention an effective amount of water is mixed with the starting material prior to forming the preform to enhance the strength of the sintered product produced therefrom. The water is mixed with the starting material at a ratio of up to about 25%, preferably between about 1% and about 10%, by weight based on the combined weight of the polymeric particles and the water of the preform. In a particularly advantageous embodiment the preform comprises about 5% by weight of water.

While not wishing to be bound by theory, it is believed that the addition of fines to the preform enhances the strength of the sintered article produced therefrom because the fines fit more readily into voids between the coarse particles and provide an increased number of fusion points. Under various conditions the fines may also completely melt and flow during the sintering process and thereby function as a binder for the coarse particles which do not completely melt. It is believed that the addition of water to the preform enhances the strength of the sintered article produced therefrom because the water functions as a plasticizer for the resin. Water is also known to be a high loss material for dielectric heating and, consequently, it is believed that the water enhances the transfer of heat to the starting mate-

rial during dielectric heating and thereby enhances the sintering process.

In the practice of the method of the present invention preforms of the starting material are sintered with dielectric heat. The exposure to dielectric heat is continued for a sufficient period of time to form sintered articles with desirable strength and porosity characteristics; the optimum exposure being dependent on the intensity of the dielectric heat, the specific starting material employed, the size and shape of the preforms, and the specific strength and porosity characteristics desired for the articles to be sintered. Effective sintering with dielectric heat is advantageously accomplished, due to the practical limitations of production requirements and other processing steps, in about one second to about two minutes, preferably about 5 to about 40 seconds. Frequencies in the high-frequency range of about 30 MHz to about 100 MHz are preferred. The intensity or power level is controlled by adjusting the height of the gap between the electrodes of the dielectric oven and the preform; specific intensity levels in relation to the gap adjustments being dependent upon the particular dielectric equipment employed. All aspects and features of performance of this sintering step can be in conformity with standard industrial dielectric heating techniques except that the extent of exposure of the preform to the dielectric heat must be carefully controlled to provide an effective sintering of the starting material resulting in the formation of sintered articles with desirable strength and porosity characteristics. Over exposure may result in sintered articles with inadequate porosity. Under exposure may result in sintered articles with inadequate strength. An advantage of sintering with dielectric heat is that heating and fusion occurs throughout the entire volume of the article substantially simultaneously and, consequently, the poor heat transfer characteristics of the preforms of the starting materials used herein are relatively inconsequential. Additionally, dielectric heating can be turned on and off instantaneously and, consequently, the sintering process of the invention can be monitored and controlled easily and precisely with reasonably simple equipment. Further, dielectric heating is efficient and thus does not throw off excessive wasted heat, and selective portions of the preform can be sintered leaving the remaining portions cool. Finally, dielectric heating equipment is easy to operate, basically long-lived, and requires relatively little maintenance.

In a particularly advantageous embodiment of the method of the present invention conventional heating is used in combination with dielectric heating. The conventional heating step may precede or follow the dielectric heating step, the sequence of these heating steps not being critical. The combination of dielectric heating and conventional heating is particularly advantageous with large, complexly configured or non-homogeneous articles where there is, in some instances, a tendency for portions of the article, particularly in the interior, to overfuse during the dielectric heating step before effective sintering has occurred at or near the surface. Under such circumstances conventional heating is advantageously employed to either (1) precondition the exterior of the article by raising its temperature to approach sintering or achieve partial sintering and thereby permit subsequent facilitated sintering with the dielectric heating step, or (2) sinter the exterior subsequent to the preconditioning or partial sintering of the exterior with the dielectric heating. The conditions under which the

conventional heating step is conducted are dependent upon the degree of heating required (i.e., whether sintering conditions or less intense conditions are to be employed) and the specific starting material used. In preferred embodiments of the invention, polymer compositions of rubber-modified nitrile resins are heated with conventional heating at a temperature in the range of about 120° C. to about 230° C., preferably about 160° C. to about 200° C., for about 2 to about 60 minutes, preferably about 15 to about 30 minutes. Oven temperatures of, for example, 260° C. that are higher than temperatures in these ranges can be employed provided residence times in the oven are limited to prevent the material being heated from exceeding these ranges.

The method of the present invention can be conducted on a batch or a continuous basis. In either case the operating parameters of each step of the process must be established within the foregoing limitations to accommodate the particular starting material employed and the particular size and configuration of the article to be sintered.

In a preferred embodiment of the present invention apparatus for a continuous process, depicted in FIG. 1, comprises extruder 10, conveyor 12, dielectric oven 14 and takeoff 16. Extruder 10 is preferably a ram or reciprocating ram extruder in which the material being extruded is advanced through the barrel and die by means of a ram or plunger rather than by a screw. In a reciprocating ram extruder two extruder units may be placed side-by-side, or end-to-end, and pulsating flow of the extrudate from alternating operated rams or plungers, aided by a valving system, is combined in a single smooth-flowing stream. Subdivided particles 20 of the starting material, which are prepared as discussed above and which advantageously include a mixture of water and/or fines, are added to the extruder 10 and extruded as a preform 22 comprising a continuous length of packed polymeric particles with a desired profile defined and determined by the extruder die. Extruder 10 is operated at a temperature below the melting point of the starting material, preferably room temperature. In instances wherein the starting material comprises rubber-modified nitrile resins, the extruder 10 is operated at a temperature below about 120° C. The preform 22 is conveyed along conveyor 12 to dielectric oven 14, the distance between extruder 10 and dielectric oven 14 not being critical. Dielectric oven 14 preferably includes a conveyor belt (not shown) communicating with conveyor 12 for carrying the preform through the dielectric oven 14. The conveyor belt must be made of a material that will not react with the starting material being sintered or be affected deleteriously by the electrode field or heat. The conveyor belt might be a low-loss material such as silicone rubber, or glass fiber, or it may be a good conductor such as stainless steel. Dielectric oven 14 is operated within the operating parameters and limitations discussed above. The production rate of extruder 10 and the speed of conveyor 12 are adjusted to permit a residence time of preform 22 in dielectric oven 14 of about one second to about two minutes, preferably about 5 to about 40 seconds.

The sintered product 24 is conveyed from dielectric oven 14 along conveyor 12 to takeoff equipment 16. The distance between the dielectric oven 14 and takeoff 16 is not critical but should be sufficient to permit adequate cooling of the sintered product 24 prior to processing in the takeoff 16. Takeoff 16 preferably includes belt units that may include cleats shaped to the profile of

the sintered product 24 to prevent distortion, and travelling saws for relatively rigid products or a flyknife cutter for relatively flexible products. The individual sintered articles 26 exit the takeoff 16 and are collected in a box 28 or other suitable collection means.

Alternate preferred embodiments of the apparatus of the present invention depicted in FIG. 1 are disclosed in FIGS. 2 and 3. Devices and articles that are the same as disclosed in FIG. 1 are identified by the same numerals in FIGS. 2 and 3. The embodiment disclosed in FIG. 2 is the same as the embodiment of FIG. 1 with the exception that conventional heating oven 18 is between extruder 10 and dielectric oven 14 to provide conventional heating of the preform 22 to yield preconditioned or partially sintered product 30 which is thereafter conveyed to dielectric oven 14 wherein the sintering process is completed. The embodiment disclosed in FIG. 3 is the same as the embodiment of FIG. 1 with the exception that conventional heating oven 18 is between dielectric oven 14 and takeoff 16 to complete the sintering of the heated or partially sintered product 32 conveyed from the dielectric oven 14. In all other respects, the embodiments disclosed in FIGS. 2 and 3 are the same as the embodiment disclosed in FIG. 1.

Oven 18 may comprise, for example, a forced air oven. Oven 18 is sufficiently elongated to permit a residence time of the material being heated of about 2 to about 60 minutes, preferably about 15 to about 30 minutes. Oven 18 may include one or a plurality of heating zones. In preferred embodiments, the starting material 20 comprises rubber-modified nitrile resins and oven 18 is operated at a temperature in the range of about 120° C. to about 230° C., preferably about 160° C. to about 200° C.

The embodiments disclosed in both FIGS. 2 and 3 comprise apparatus for use in a sintering process employing both dielectric heating and conventional heating techniques and are advantageously employed with continuous preforms having large or complexly configured cross-sectional designs or profiles. In the embodiment disclosed in FIG. 2, the preform 22 is preconditioned in oven 18 by having its temperature raised to a point approaching sintering or to achieve partial sintering prior to conveyance to the dielectric oven 14 to complete the sintering process. In FIG. 3, the dielectric oven 14 functions to either precondition the preform 22 by heating it to a temperature approaching the sintering temperature or to partially sinter the preform, the sintering process subsequently being completed in oven 18.

The sintered articles or products produced by methods in accordance with the invention comprise porous structures with properties that are dependent upon the specific sintering conditions used and the particular starting material employed. In preferred embodiments of the invention, porous structures comprising rubber-modified nitrile resins are produced that have a specific gravity in the range of about 0.3 to about 1.2, preferably about 0.5 to about 1.0, and water absorption capacities of between about 10% and about 150% by weight, based on the weight of said article, preferably about 30% to about 100% by weight. Sintered articles made in accordance with the present invention from such rubber-modified nitrile resins are substantially chemically resistant and hydrophillic in character, and have applications, for example, as filters, diffusers, applicator rolls, aerators, battery separators, and marking pen points.

By way of further illustration of the invention, reference may be made to the following examples. Unless



otherwise indicated, all parts and percentages are by weight.

In the following examples various methods were used to identify and evaluate specific characteristics of the sintered articles produced in accordance with the invention.

**Specific Gravity**—Weigh the sample (in grams) and measure its dimensions (in centimeters). Divide the weight by the sample volume.

**Water Absorption**—Using the same sample, soak the sample in water for one minute and weigh the wet sample after surface water is knocked off by hand. The percent water absorbed is the weight of water absorbed divided by the original sample weight multiplied by

supplied by The Standard Oil Company (Ohio), Cleveland, Ohio, is recovered from its emulsion in powder form and separated using Tyler 120–170 mesh screens. The separated polymer is formed into discs in 1½ inch diameter molds using a preform pressure of 5,000 PSI at room temperature. In the example where water is added to the polymer (Example 8) the addition is made prior to filling the mold and the amount indicated is percentage by weight based on the weight of the polymer. Conventional or oven heating is accomplished using a forced air oven at 135° C. Dielectric heating is accomplished using a La Rose 8 V, 320 milliamp microwave oven set at 1½ inch height operating at 71.5 MC. Cooling is accomplished in air at room temperature.

Example	Water	Heat Source	Time	Pressure Drop (mm. Hg)	Specific Gravity	Water Absorption	Break Load Kg	Flexural Strength (Kg/cm <sup>2</sup> )
1	No	dielectric	30 sec.	680	0.728	44%	6.5	23.3
2	No	oven	15 min	675	0.707	48%	4.3	14.1
3	No	oven	22.5 min	675	0.694	40%	5.7	17.2
4	No	oven	30 min	680	0.687	39%	8.8	26.6
5	No	dielectric/oven	10 sec./7.5 min	680	0.659	49%	3.4	10.4
6	No	dielectric/oven	12.5 sec./11.25 min	680	0.702	47%	6.4	20.9
7	No	dielectric/oven	15 sec./15 min	650	0.683	49%	7.5	22.4
8	5%	dielectric/oven	12.5 sec./11.25 min	706	0.780	27%	8.2	30.4

100.

**Flexural Strength**—The samples used in the water absorption tests are allowed to dry for three days and used for determining strength. The sample is placed across a span and the load to break the sample is measured by a load cell or scale (similar to the method described in ASTM D790). The flexural strength is calculated using the following equation:

$$\text{Flexural strength} = \frac{3P \times L}{4bh^2}$$

where

P=span

L=load(kg)

b=the beam width

h=the beam thickness

**Pressure Drop**—A porosity test unit for measuring the pressure drop across a porous disc sample consists of a first tube connected to a water or air supply and a second tube connected to a vacuum pump, the first and second tubes being connected to each other with a ¼ inch union. A space for the disc sample is provided in the union. Connected to the second tube between the union and the vacuum pump is a sealed mercury manometer. The union is closed without a sample and the vacuum turned on full flow. The mercury manometer shows a small amount of pressure drop for the empty system (high value). The union is opened and the sample space is plugged. The manometer shows a low value (minimum leakage). The disc sample is gasketed by painting a PVC plastisol on the edge and ¼" in from edge, placed inside the opened union which is resealed using firm pressure. The vacuum is turned on (pulling air through the disc sample) and the mercury manometer is read. The difference between the reading with the sample in place and the empty system reading is the pressure drop.

#### EXAMPLES 1 TO 8

In Examples 1 to 8, 2 gm. samples of Barex® 210 polymer, a rubber-modified nitrile resin based polymer

The foregoing examples demonstrate that the properties of the rubber-modified nitrile resin polymer composition sintered using dielectric heat for 30 seconds (Example 1) are comparable or superior to the properties of the same polymer sintered for 15 to 30 minutes (Examples 2 to 4) using a forced air oven under otherwise equivalent conditions. These examples also demonstrate that dielectric heating can be used effectively in combination with conventional heating to sinter preforms of rubber-modified resin compositions. (Examples 5 to 8). These examples demonstrate that the addition of water improves the strength of a product sintered with a method using dielectric heat (Examples 6 and 8). Finally, these examples demonstrate that the preforms of rubber-modified nitrile resin compositions tested herein have sufficiently high loss factors to be effectively heated with dielectric heat.

In the foregoing examples, optimum properties of porosity for various applications such as, for example, certain types of filters wherein relatively porous structures are required, were not achieved under the specific conditions employed due to the fact that the polymer recovered from the emulsion was relatively porous in nature. Consequently, the pressure exerted during the preparation of the preforms compacted the particles to the point that there were insufficient interstices to permit the formation of relatively porous preform structures. Sintered articles with relatively porous structures can be produced if the polymeric powder utilized in the above examples is first melted, for example in an extruder or on a hot mill, then allowed to cool followed by the step of chopping or grinding the cooled melt into cylindrical or cube forms. The melt may be cut as it emerges from the extruder die and then chilled before it fuses; this results in thin cylindrical forms referred to as a "lens" or "fish eye". Lens grade polymers are particularly suited for feeding extruders or molding machines because of their dense nature and free flowing characteristics. However, to be useful in the sintering techniques of the present invention, these grades must be reduced in size to powder form. The resulting powder is

significantly more dense and less porous than the powder originally recovered from the emulsion.

### EXAMPLE 9

Densified lens grade Barex® 210 polymer is ground in a Wiley mill and separated using Tyler 70-170 mesh screens. The separated polymer is formed into a disc in a 1½ inch diameter mold using a preform pressure of 5000 PSI at room temperature. The resulting preform is heated using a combination of dielectric heat for 15 seconds and conventional heat for 15 minutes in the same manner as in the above examples. Cooling is accomplished in air at room temperature. The resulting sintered article exhibited the following characteristics:

Pressure drop (mm. Hg.)	7.9
Specific gravity	0.48
Water absorption (%)	80
Break Load (Kg)	0.6
Flexural Strength (Kg/cm <sup>2</sup> )	2.0

### EXAMPLE 10

Two grams of the Barex® 210 ground lens polymer of Example 9 are mixed with 0.2 grams water and formed into discs 1½ inch diameter using a preform pressure of 4000 PSI at room temperature in the same manner as Examples 1-9. The preforms are sintered using dielectric heating for 15 seconds and forced air oven heating at 135° C. for 30 minutes. The resulting sintered article exhibited the following characteristics:

Pressure drop (mm. Hg.)	8.7
Specific Gravity	0.56
Water Absorption (%)	68
Break Load (Kg)	1.95
Flexural Strength (Kg/cm <sup>2</sup> )	5.1

### EXAMPLES 11 AND 12

In the following examples preforms of Barex® 210 polymer are formed using the indicated preform pressure to form discs having diameters of 1½ inches and thicknesses of 0.15 inches. The particle size range of the coarse polymeric particles is Tyler 70-170 screen mesh. Ten percent by weight of the preforms are fines, i.e., particles that pass through a No. 240 Tyler mesh sieve. The preforms are heated using dielectric heating for 15 seconds and forced air oven heating at 135° C. for 30 minutes in the same manner as in Examples 1 to 10.

	Example 11	Example 12
Preform Pressure, PSI	1000	4000
Specific Gravity	.63	.71
Pressure Drop (mm Hg)	8.9	14.1
Water Absorption	72%	68%
Strength (Kg)	3.0	4.0
Flexural Strength (Kg/cm <sup>2</sup> )*	14	23.7

\*Adjusted for actual dimensions.

These examples demonstrate that the use of a blend of fines with coarse particles provides for improved porosity. They also demonstrate that improved strength can be obtained with higher preform pressures.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification.

Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

We claim:

1. A method for producing a sintered porous polymeric article from a polymeric material with a sufficiently high loss factor for effective dielectric heating comprising:

forming a preform comprising a plurality of discrete polymeric particles compressed together in a predetermined shape; and

sintering said preform to form said article, said sintering step including the step of heating said preform using dielectric heating, said sintering step being conducted for a sufficient period to provide said article with desired strength and porosity.

2. The method of claim 1 wherein said sintering step includes the step of heating said preform using conventional heating.

3. The method of claim 2 wherein said conventional heating step precedes said dielectric heating step.

4. The method of claim 2 wherein said dielectric heating step precedes said conventional heating step.

5. The method of claim 1 wherein said preform includes up to 100% by weight coarse particles, said coarse particles being small enough to pass through a No. 16 Tyler mesh sieve.

6. The method of claim 5 wherein said coarse particles are small enough to pass through a No. 70 Tyler mesh sieve.

7. The method of claim 1 wherein said preform includes up to 100% by weight fines, said fines being small enough to pass through a No. 240 Tyler mesh sieve.

8. The method of claim 1 wherein said preform comprises between about 5% to about 25% by weight particle fines.

9. The method of claim 1 wherein said preform comprises up to about 25% by weight of water.

10. The method of claim 9 wherein said preform comprises about 1% to about 10% by weight of water.

11. The method of claim 9 wherein said preform comprises about 5% by weight of water.

12. The method of claim 1 wherein said preform is formed in a mold with a pressure of up to about 10,000 pounds per square inch.

13. The method of claim 12 wherein said preform is formed in a mold with a pressure in the range of about 100 to about 4000 pounds per square inch.

14. The method of claim 1 wherein said dielectric heating step is conducted with microwaves of electromagnetic energy having a frequency in the range of about 890 to about 10,000 MHz.

15. The method of claim 2 wherein said conventional heating is conducted at a temperature in the range of about 120° C. to about 230° C.

16. The method of claim 15 wherein said conventional heating is conducted at a temperature in the range of about 160° C. to about 200° C.

17. The method of claim 1 wherein said dielectric heating step takes about one second to about two minutes.

18. The method of claim 17 wherein said dielectric heating step takes about 5 to about 40 seconds.

19. The method of claim 2 wherein said conventional heating step takes about two minutes to about 60 minutes.



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20. The method of claim 19 wherein said conventional heating takes about 15 to about 30 minutes:

21. The method of claim 1 wherein said dielectric heating step is conducted with high-frequency waves of electromagnetic energy having a frequency in the range of about one to about 200 MHz.

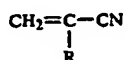
22. The method of claim 1 wherein the loss factor of said polymeric material exceeds about 0.08.

23. The method of claim 1 wherein the loss factor of said polymeric material exceeds about 0.2.

24. The method of claims 1 or 2 wherein said polymeric material comprise a rubber-modified nitrile resin.

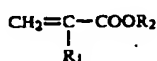
25. The method of claim 24 wherein said polymeric material comprise a resin resulting from the polymerization of 100 parts by weight of

(a) at least 50% by weight of at least one nitrile having the structure



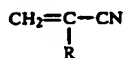
wherein R is hydrogen, a lower alkyl group having from 1 to 4 carbon atoms, or a halogen, and

(b) up to 50% by weight based on the combined weight of (a) and (b) of an ester having the structure

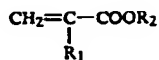


wherein R<sub>1</sub> is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or a halogen, and R<sub>2</sub> is an alkyl group having from 1 to 6 carbon atoms, in the presence of from 1 to 40 parts by weight of

(c) a polymer of about 50% to 100% by weight of a conjugated diene monomer selected from the group consisting of butadiene and isoprene and about 0% to 50% by weight of at least one member selected from the group consisting of styrene, an olefinically unsaturated nitrile having the structure



wherein R has the foregoing designation and an ester having the structure



wherein R<sub>1</sub> and R<sub>2</sub> have the foregoing designations.

26. The method of claim 25 wherein (a) is acrylonitrile.

27. The method of claim 25 wherein (b) is methyl acrylate.

28. The method of claim 25 wherein (c) is a copolymer of butadiene and acrylonitrile.

29. A continuous process for forming sintered porous polymeric articles from a polymeric material with a sufficiently high loss factor for effective dielectric heating comprising:

forming a preform comprising a continuous length of packed discrete polymeric particles of said polymeric material;

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sintering said preform in a sintering step comprising the step of heating said preform using dielectric heating; and

comminuting the sintered preform from the previous step to form discrete sintered porous polymeric articles.

30. The method of claim 29 wherein said sintering step includes the step of heating said preform using conventional heating.

31. The method of claim 30 wherein said conventional heating step precedes said dielectric heating step.

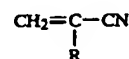
32. The method of claim 30 wherein said dielectric heating step precedes said conventional heating step.

33. The method of claim 29 wherein said forming step comprises extruding discrete polymeric particles to form said preform.

34. The method of any of claims 29-33 wherein said polymeric material is a rubber-modified nitrile resin.

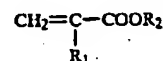
35. The method of any of claims 29-33 wherein said polymeric material comprises a resin resulting from the polymerization of 100 parts by weight of

(a) at least 50% by weight of at least one nitrile having the structure



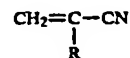
wherein R is hydrogen, a lower alkyl group having from 1 to 4 carbon atoms, or a halogen, and

(b) up to 50% by weight based on the combined weight of (a) and (b) of an ester having the structure

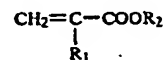


wherein R<sub>1</sub> is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or a halogen, and R<sub>2</sub> is an alkyl group having from 1 to 6 carbon atoms, in the presence of from 1 to 40 parts by weight of

(c) a polymer of about 50% to 100% by weight of a conjugated diene monomer selected from the group consisting of butadiene and isoprene and about 0% to 50% by weight of at least one member selected from the group consisting of styrene, an olefinically unsaturated nitrile having the structure



wherein R has the foregoing designation and an ester having the structure



wherein R<sub>1</sub> and R<sub>2</sub> have the foregoing designations.

36. The method of claim 35 wherein (a) is acrylonitrile.

37. The method of claim 35 wherein (b) is methyl acrylate.

38. The method of claim 35 wherein (c) is a copolymer of butadiene and acrylonitrile.

\* \* \* \* \*

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(45) Date of Patent: **Aug. 7, 2001**

(54) **MANUFACTURING METHOD OF A HIGHLY CONDUCTIVE  
POLYTETRAFLUOROETHYLENE SHEET**

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264/127; 264/146; 264/175; 264/150

(58) Field of Search ..... 264/104, 105,  
264/125, 127, 175, 176.1, 209.1, 210.1,  
211, 213, 145, 146, 148, 150, 118, 119;  
428/421

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(57) **ABSTRACT**

This invention concerns a method of manufacturing a highly conductive polytetrafluoroethylene sheet; a method of manufacturing a highly conductive unsintered polytetrafluoroethylene sheet; and a method of manufacturing a highly conductive sintered sheet. In the first method, a paste of polytetrafluoroethylene powder admixed with conductive substance and extrusion lubricant is extruded to preform an unsintered tube-like material, and at least one place on the circumference of this extruded material, the material is cut open longitudinally and the resulting sheet is calendered if necessary. The second method includes a sintering process for the sheet. This invention also concerns a highly conductive polytetrafluoroethylene sheet having a wide-width and long-length, which is obtained by the above-mentioned method. This sheet is not less than 170 mm in width and has variance of volume resistivity (conductivity) in the longitudinal direction, 10% or less, preferably 7% or less in the cross direction. This invention can provide a highly conductive wide-type PTFE sheet whose conductivity in the longitudinal direction is nearly uniform in the cross direction.

**6 Claims, 4 Drawing Sheets**

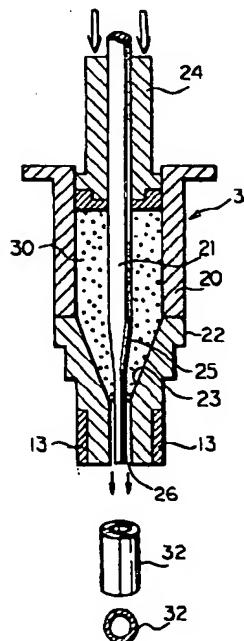


FIG. 1

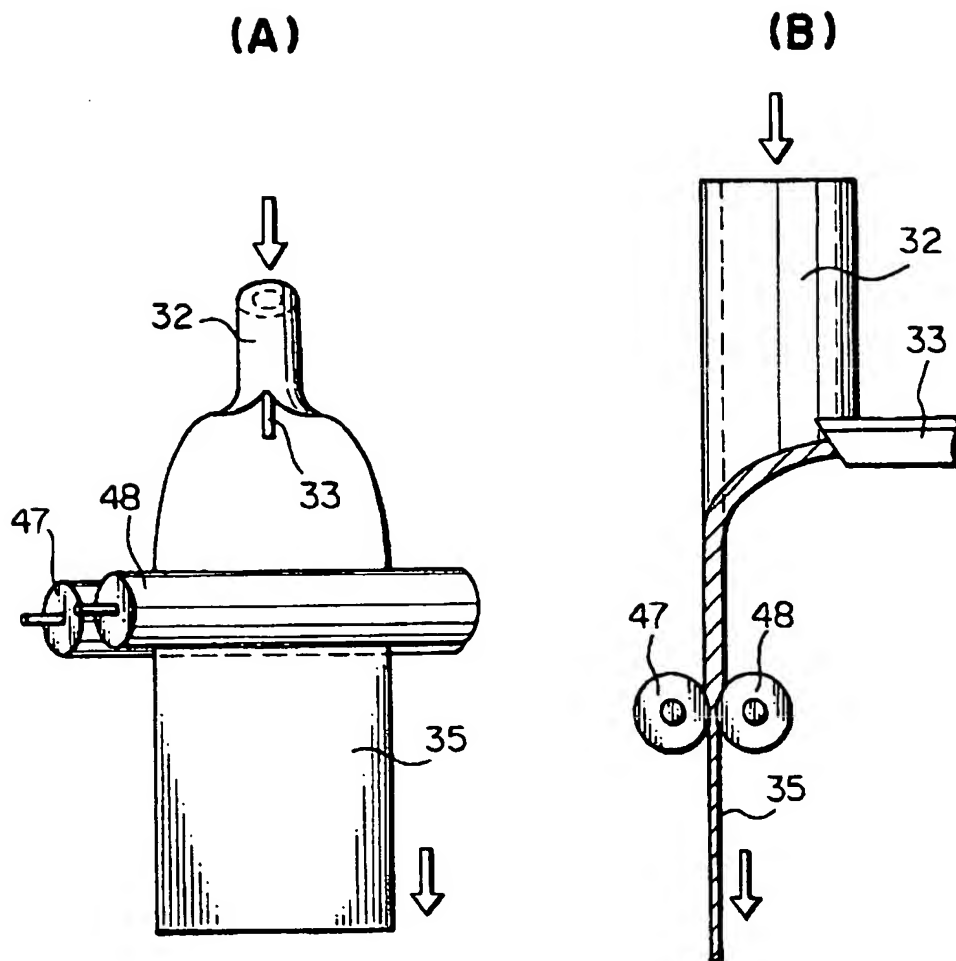


FIG. 2

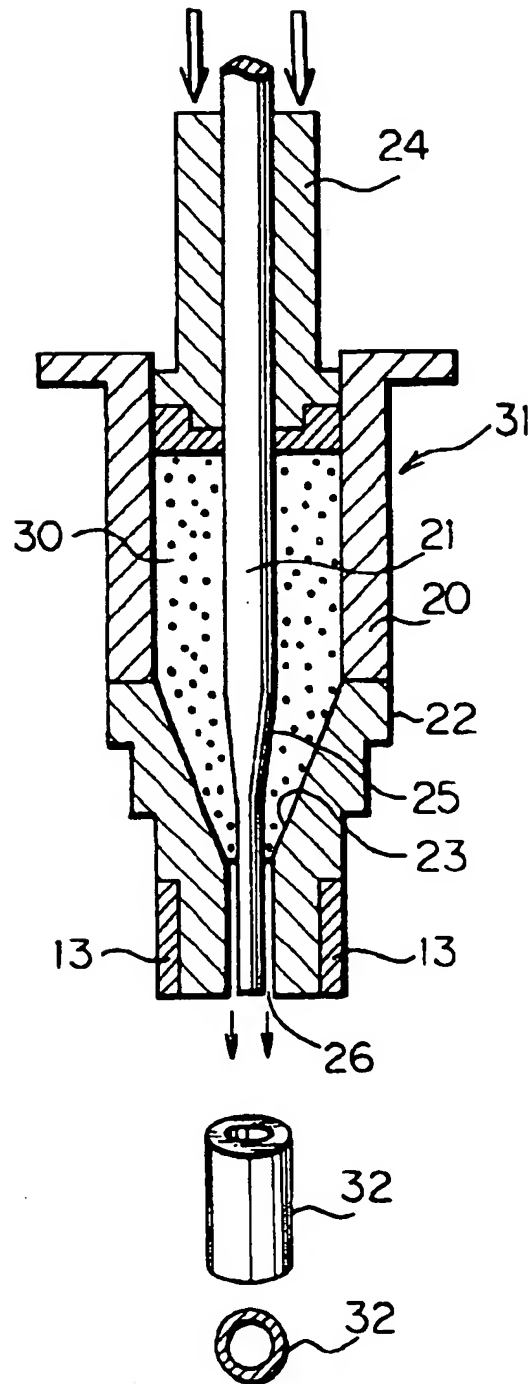


FIG. 3

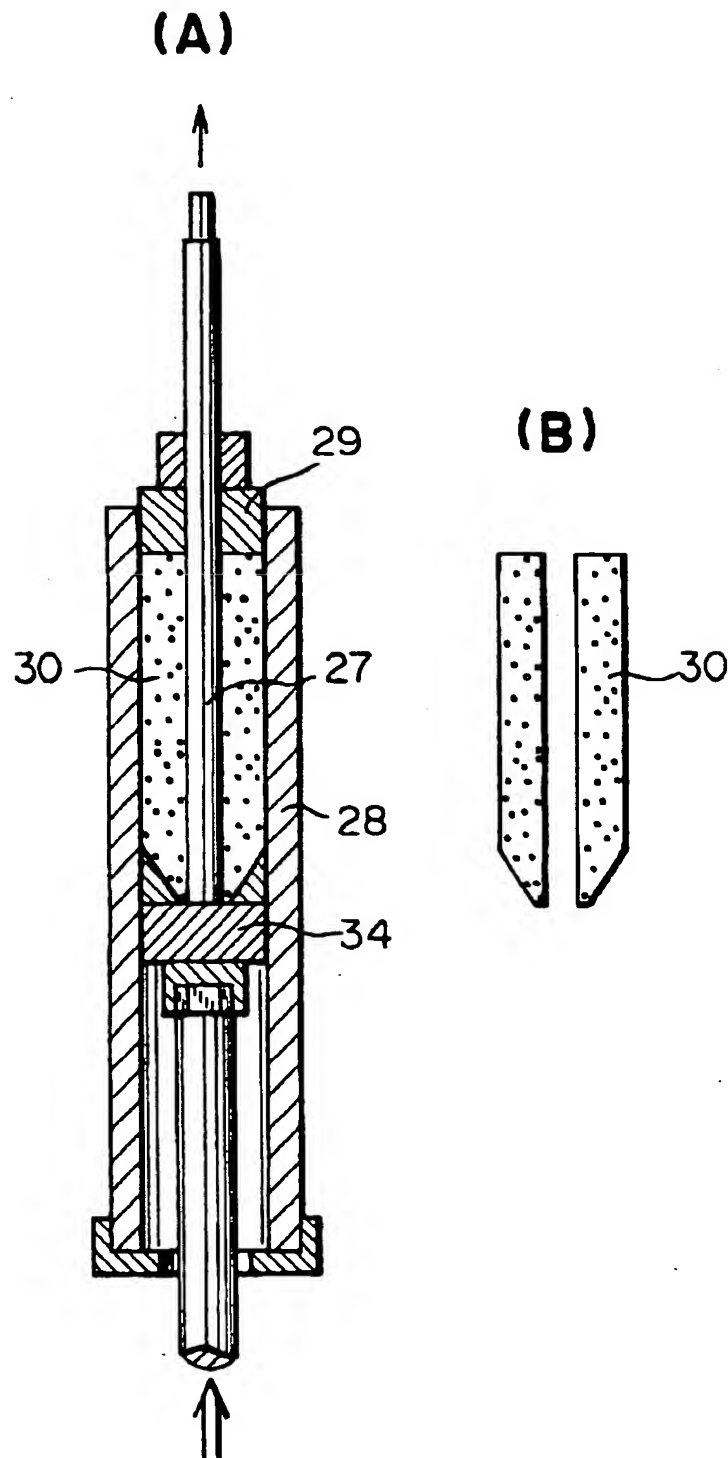


FIG. 4

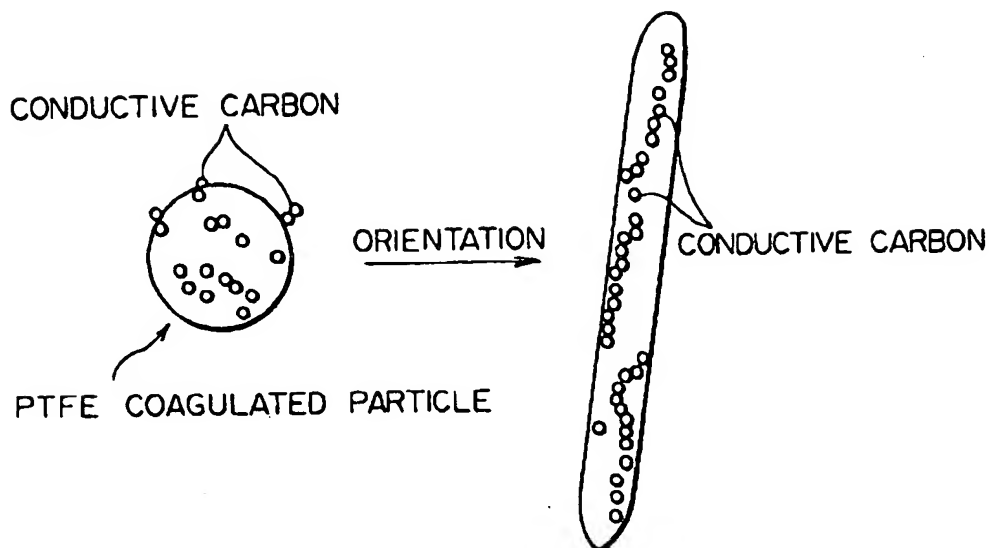
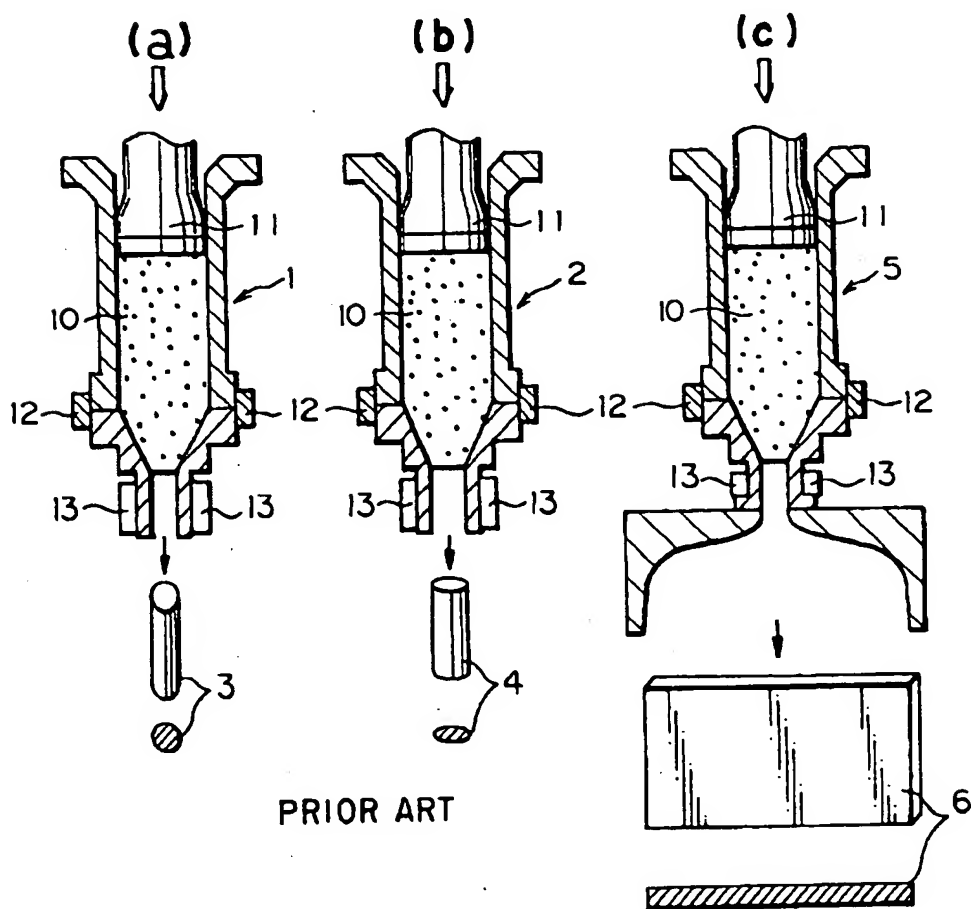


FIG. 5



# MANUFACTURING METHOD OF A HIGHLY CONDUCTIVE POLYTETRAFLUOROETHYLENE SHEET FIELD OF INDUSTRIAL APPLICATION

This invention relates to a manufacturing method of a highly conductive polytetrafluoroethylene sheet (hereinafter called PTFE sheet) which is suitable for a raw material of sheet-type heating elements and electrodes of primary batteries, secondary batteries and fuel cells, especially highly conductive PTFE sheet which is suitable for a raw material of highly conductive PTFE sheet having a wide-width and a long-length. This invention also relates to a highly conductive PTFE sheet which conductivity in the longitudinal direction is nearly uniform in the cross direction.

## PRIOR ART

Such a highly conductive PTFE sheet has been conventionally manufactured by the following method. PTFE prepared by the suspension polymerization method is ground into powder with a particle size of 20–40  $\mu\text{m}$ . This powder is mixed with conductive carbon (5–15 weight percent),

The resulting mixture is placed in a certain metal mold for compression preforming at 400–600  $\text{kgf/cm}^2$ . The molded block is sintered at 380° C. for 5–10 hours. Thus obtained block is shaved into thin sheets.

These sheets have volume resistivity of  $10^2$ – $10^4$   $\Omega\text{-cm}$  which is low conductive. The surface of this low conductive sheets lack smoothness, because scratches are formed on the surface during the shaving process.

PTFE sheet can be also produced by another method. Aqueous dispersion containing PTFE with a particle size of 0.15–0.35  $\mu\text{m}$  is obtained by the emulsion polymerization method.

A nonionic surface-active agent, water and carbon are kneaded in a ball mill to prepare the conductive paste. The aqueous dispersion and the paste are mixed to prepare a coating material. This coating material is then coated onto a plate. After drying, the plate is sintered at 380° C. for approximately 15 minutes. The coated film separated from the plate can be obtained as a conductive sheet.

The volume resistivity of the sheet produced by this method ranges from approximately  $10^0$   $\Omega\text{-cm}$  to  $10^1$   $\Omega\text{-cm}$  if conductive carbon is added at 8–30 weight percent. The volume resistivity depends on the amount of conductive carbon added, but the conductivity of this sheet is not yet sufficient. And, producing a sheet having a thickness exceeding 60  $\mu\text{m}$  and without crack by this technique is extremely difficult.

Therefore, highly conductive PTFE sheet is conventionally produced by the following method. A paste of PTFE powder admixed with conductive substance and extrusion lubricant is extruded through dies as shown in FIG. 5(a) and FIG. 5(b). These extruded materials are then calendered and sintered to the final products.

According to FIG. 5(a) and FIG. 5(b), said paste 10 is extruded through cylindrical die 1(a) or oval body type die 2(b) into rod-like unsintered extruded material 3 or 4. These extruded materials are calendered.

The highly conductive PTFE sheet having a wide-width and a long-length is obtained by the following method. As shown in FIG. 5(c), the paste is extruded through T die 5. This extruded sheet 6 is calendered. Although the technique is not illustrated in figure, extruded sheet 6 can be also calendered by a multistage calendering roll (d). In FIGS. 5, 11, 12 and 13 show respectively a ram, a fixing ring and a heater.

However, the above-mentioned producing techniques (a) and (b) can provide sheets as commercial products having the maximum width of 160 mm because the width of such obtained products are restricted. When the width of the products are larger, their conductivity in the longitudinal direction decreases and loses uniformity in the cross direction. The conductivity in the longitudinal direction of the above-mentioned techniques (c) and (d) is low and a multistage calendering roll or a roll with large diameter is needed to produce these sheets.

[A roll with large diameter (e.g. 500 mm $\phi$ ) or the like is preferably used to produce PTFE sheets with higher conductivity.] These techniques require complicated and large equipment, thus increasing the cost.

## OBJECT OF THE INVENTION

The objects of this invention are to provide highly conductive PTFE sheet which is useful for a raw material of sheet-type heating elements and electrodes of primary batteries, secondary batteries and fuel cells, and to provide a producing method thereof. This highly conductive PTFE sheet requires the following conditions:

- (1) Wide width
- (2) High conductivity in the longitudinal direction
- (3) Conductivity in the longitudinal direction is nearly uniform in the cross direction.

## CONSTRUCTION OF THE INVENTION

This invention concerns a method to manufacture highly conductive PTFE sheets. According to this method, A paste of PTFE powder admixed with conductive substance and extrusion lubricant is extruded to prepare an unsintered tube-like material. At least one place on the circumference of this unsintered tube-like extruded material, the material is cut open longitudinally and the resulting sheet is further calendered if necessary. This invention also concerns a method to manufacture highly conductive PTFE sheets by sintering the sheets produced by the above-mentioned method.

(These methods are regarded as the invented manufacturing methods.)

These invented manufacturing methods can be applied to the manufacturing of highly conductive PTFE sheets being not less than 170 mm in width and also those being less than 170 mm in width. These invented manufacturing methods can be applied to the manufacturing of highly conductive PTFE sheet having a wide-width and a long-length (the invented sheet) which is not less than 170 mm in width and whose variance of volume resistivity (conductivity) in the longitudinal direction is 10% or less in the cross directions, preferably 7% or less.

(The definition of the variance is described later.)

According to these invented manufacturing methods, at least one place on the circumference of the tube-like extruded material, the material is cut open longitudinally to a sheet. This sheet is calendered if necessary so that PTFE particles are sufficiently oriented in the longitudinal direction (on the internal and external surfaces of the extruded material or in the whole extruded material). This orientation is carried out during the calendering process. Therefore, the mixed conductive substances such as conductive carbon are arranged lengthwise in nearly straight lines. This parallel arrangement of conductive substances is indispensable for producing highly conductive PTFE sheet with conductivity in the longitudinal direction is nearly uniform in the cross direction.

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The PTFE sheets with following excellent properties of the invention can be obtained with high reproducibility by the invented manufacturing methods. Those with uniform exothermic properties are used for sheet-type heating elements, while those with water repellent properties are used for the electrodes of primary batteries, secondary batteries and fuel cells.

These invented sheets are highly conductive which are not less than 170 mm in width and whose variance of volume resistivity (conductivity) in the longitudinal direction is 10% or less, preferably 7% or less.

PTFE, which is used for a raw material of the invented method and sheet, can be preferably obtained usually from PTFE aqueous dispersion prepared by emulsion polymerization of tetrafluoroethylene (hereinafter called TFE).

PTFE includes not only PTFE itself but also modified PTFE which are modified by PTFE modifying monomers.

PTFE modifying monomers include fluorine-containing unsaturated monomers except for TFE, such as fluoroalkyl vinyl ethers expressed by the following chemical formulas:



where,

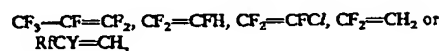
"X" indicates hydrogen, fluorine or chlorine and "n" indicates an integer ranging from 1 to 6,

or,



where,

"m" and "l" are integers ranging from 0 to 4, that are never zero simultaneously.



where,

"RP" indicates straight or branched polyfluoroalkyl group having 3 to 21 carbon atoms; Y indicates hydrogen or fluorine atoms. Such fluorine-containing unsaturated monomers are generally added in amounts that do not exhibit melt-flow properties. The adequate amount is adjusted depending on the types of modifying monomers. For example, some modifying monomers are added at less than 2 percent by weight, preferably 0.0-1 percent by weight of PTFE.

In order to prepare paste of PTFE powder used in the present invention, PTFE-containing aqueous dispersion obtained by the above-mentioned emulsion polymerization of TFE is mixed with the following substances:

(1) conductive substances mentioned later

or,

(2) these conductive substances and the extrusion lubricants mentioned later.

The mixture is stirred to coagulate. In the second case, the coagulated substance obtained is directly used as paste of PTFE powder (refer to WO95/23178).

In the first case, the coagulated substance obtained is dried, then the dried material can be used for paste of PTFE powder when mixed with the extrusion lubricants.

The conductive substances used in the present invention include conductive carbon, carbon fiber and metal particles. Of these, conductive carbon is most preferable.

The amounts of conductive substances to be added are adjusted depending on the following use. If PTFE sheet is

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used for sheet-type heating elements, conductive substances are generally added at 15-50 percent by weight of PTFE. If PTFE sheet is used for the above-mentioned batteries, conductive substances can be generally added at more than 50 percent by weight of PTFE.

The extrusion lubricants used in the present invention are white oil, isoper, smoil and naphtha. They are generally added in the amounts ranging 10 to 60 percent by weight of PTFE and conductive substance.

#### PREFERRED EMBODIMENTS OF THE INVENTION

According to the present invented manufacturing methods, for example, the paste of PTFE powder is molded preparatorily with the compression molding machine shown in FIG. 3(A). A preform 30 is set in the ram extruder shown in FIG. 2. By extrusion molding of the preform 30 an unsintered PTFE tube-like extruded material 32 is obtained.

A ram extruder 31 which can be used for the present invented manufacturing methods is shown in FIG. 2. It consists of a cylinder 20, a mandrel 21, a die 22, a tapered part 23 and a pressure ram 24. The mandrel 21 is set in the center of the cylinder 20. The die 22 having a tapered part 28 is fixed which is set at the taper 25 side of the mandrel 21 in the cylinder 20. The passage for the preform 30 tapers off to an outlet 26. The ram 24 is set on the opposite side of the tapered part 23.

Although the above-mentioned extrusion pressure ranges from approximately 70 to 300 kgf/cm<sup>2</sup>, the pressure is adjusted to the level according to the reduction ratio (hereinafter called R.R.), which is the ratio between the cross section (R) of the cylinder 20 of the extruder 31 and the cross section (R') at the exit of the die 22. Generally, this ratio is adjusted to 10-200 and the extruding pressure rises when R.R. increases.

If conductive carbon is used as the conductive substance in the extrusion process, it is supposed that as shown in FIG. 4, all the parts of the material to be extruded is easily oriented so that PTFE particles are stretched lengthwise and the carbon structure is oriented.

Preform 30 which is obtained from the paste of PTFE powder can be set in the extruder 31 by the following method. As shown in FIG. 3(A) and FIG. 3(B), the preform 30 is obtained by pressing with a pressure ram 34 from the opposite side of a cap 29 inside a cylinder 28 with a mandrel 27 in the center. This preform 30 can be inserted into the cylinder 28.

This preforming is usually carried out so that the material to be extruded can be easily inserted into the cylinder. The preferable pressure for preforming ranges from 10 to 50 kgf/cm<sup>2</sup>.

The unsintered tube-like material 32 is extruded from the extruder 31.

One or more places (in this case, one place on the circumference of this extruded material) are cut open with a cutter 33 etc. in the longitudinal direction to prepare a sheet, as shown in FIG. 1. This sheet can be set between a calendaring roll 47 and a calendaring roll 48 for rolling if necessary. A highly conductive sheet 35 having a wide-width can be obtained by this rolling process.

The number of out made at the unsintered extruded tube-like material determine the number of sheet to be developed:

(1) One sheet is developed by one cut.

(2) Two sheets are developed by two cuts.

(3) More than three sheets are developed by three cuts or more,



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In this case, the above case (1) is mainly explained. In the remaining two cases, (2) and (3), however, highly conductive sheets for a target can be obtained in a similar manner.

For example, in case (1), a cut is made with a cutter on the circumference of the unsintered tube-like material to develop a sheet. This sheet is reeled up as a material for the invented highly conductive PTFE sheet. This sheet is soaked in hot water at, for example, 80° C. for heating and set in the roll if necessary. In the present invention, it is preferable that the sheet be extended by the calendaring roll in the longitudinal direction by 1 to 10 times while it is extended in the cross direction by 1 to 3 times.

In the present invention, the thickness of the extruded sheet material generally ranges from 0.3 mm to 5 mm. This unsintered tube-like material is cut open and the developed sheet is calendered and extended longitudinally by 1 to 10 times and transversely by 1 to 3 times if necessary. This sheet is generally inserted between a couple of calendaring rolls rotatable each other. In order to roll the sheet easily, these calendaring rolls are heated to a temperature ranging from room temperature to 100° C.

The thickness of the calendered sheet is preferably from approximately 0.05 mm to 2 mm. The calendaring process can be carried out one time or more.

The rolled sheet is then heated from 100 to 260° C. by the ordinary method to remove the extrusion lubricant and unsintered sheet is obtained. The resultant sheet has a high elasticity.

Accordingly a wide and long sheet of polytetrafluoroethylene which has high conductivity in the longitudinal direction and nearly uniform conductivity in the cross direction is obtained. Although the volume resistivity of this sheet in the longitudinal direction generally ranges from  $10^{-3}$   $\Omega$ -cm to  $10^5$   $\Omega$ -cm, preferably its volume resistivity should be adjusted to the level from  $10^{-3}$   $\Omega$ -cm to  $10^0$   $\Omega$ -cm.

In order to enhance the mechanical strength and the conductivity of the PTFE sheet, the sheet is sintered at a temperature of from the melting point (327° C.) of PTFE to its decomposition temperature (400° C.) for 1 to 30 minutes.

The highly conductive sheet produced by the present invented methods is not less than 170 mm in width and has volume resistivity (conductivity) ranging from  $10^{-3}$   $\Omega$ -cm to  $10^5$   $\Omega$ -cm in the longitudinal direction, preferably ranging from  $10^{-3}$   $\Omega$ -cm to  $10^0$   $\Omega$ -cm, and its variance of volume resistivity (conductivity) in the longitudinal direction is 10% or less, preferably 7% or less in the cross direction.

This highly conductive wide-type PTFE sheet shows remarkable uniformity in the cross direction of conductivity in the longitudinal direction. Because of its excellent property, this highly conductive PTFE sheet can be practically applied to various fields as a sheet-type heating element. Moreover, this highly conductive PTFE sheet is a useful material for the electrodes of primary batteries, secondary batteries and fuel cells. Consequently, this highly conductive PTFE sheet is useful for industry.

This producing technique of the invention requires only simple and small equipment (a calendaring roll with small-diameter is available), which reduces the cost because of the compactness of the equipment. Beside these advantages, this highly conductive PTFE sheet has the following excellent properties. Although the edges of sheets produced by conventional methods easily become wavy, be cracked and serrated, this new sheet suffers virtually none of these defects. The edge of this new sheet forms an almost straight line and the loss of the sheet is decreased, which significantly improves the yield of the sheet.

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## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1: An oblique sketch (A) of the processes of cutting and calendering of the tube-like extruded material prepared by this invented method and a sectional view (B).

FIG. 2: A cross sectional view showing the extruder to be used for extruding, in a tube form, the preform of a paste of PTFE powder prepared by this invented method and an oblique sketch and a sectional view of the unsintered tube-like material.

FIG. 3: A sectional view of the preforming machine to be used for preparing the preform to be inserted into the extruder (A) and an oblique sketch of the preform (B).

FIG. 4: A schematic sketch showing the orientation of PTFE particle in the surface of the extruded material.

FIG. 5: Oblique sketches and sectional views of various types of conventional dies and extruded materials.

The numbers used in the figures correspond to the following functional parts.

- 1,2,5,31: extruder (mold or die)
- 3,4,6,32: unsintered extruded material
- 10,80: preform
- 11,24: extruding ram
- 13: heater
- 20,28: cylinder
- 21: mandrel (used for extrusion)
- 22: die
- 28,25: taper
- 27: mandrel (used for preforming)
- 33: cutter (knife)
- 84: preforming pressure ram
- 35: conductive sheet
- 47,48: calendaring roll

## EXAMPLES

This invented method will be explained in more detail with reference to the following examples.

### Examples 1 to 4

PTFE fine powder containing conductive carbon powder (HS500, Asahi Carbon Co., Ltd.) (25 weight percent) was mixed with white oil (35 weight percent) as a extrusion lubricant. Pressure (50 kgf/cm<sup>2</sup>) was applied to the resulting mixture for preforming.

Under the following conditions, the preformed materials were extruded by the extruder shown in FIG. 2.

Internal diameter of the cylinder 20: 76 mm (Examples 1, 3, 4); 102 mm (Example 2)

Diameter of the mandrel 21: 30 mm

Die outlet diameter: External diameter 21.5 mm, Internal diameter 20.1 mm (Example 1)

External diameter 100 mm, Internal diameter 99 mm (Example 2)

External diameter 45 mm, Internal diameter 43.8 mm (Example 3)

External diameter 45 mm, Internal diameter 43.9 mm (Example 4)

In these cases, the extruding part of the extruder was heated to 50–80° C. and the material was extruded to a tube-like form under the pressure of 70–150 kgf/cm<sup>2</sup>. Then a cut was carried out on the circumference of the tube-like material with a cutter and the material was cut open to a sheet.

The sheet was calendered through a calendaring roll with 500 mm diameter at 60° C. into a 120  $\mu$ m thick sheet. The

lubricant was removed at 160–260° C. As tensile force was then applied in the rolling direction, the sheet was sintered in a furnace at 380° C. for 2 minutes.

Under various extruding and calendering conditions, the volume resistivity of the resulting sheet of each example was measured and the states of the each sheet were carefully observed. The results are summarized in Table 1.

In order to determine the volume resistivity, an AC voltage was applied and the electric current and size of the each sheet were measured. A test sample of highly conductive PTFE sheet (width: 10 mm, longitudinal length: 220 mm) was prepared by cutting the resulting sheet. In this case, only in Example 1 the sheet was cut from the end of the width into 9 test samples of 10 mm width spaced at intervals of 0.625 mm along the cross direction. Two copper foil electrodes of 10 mm width were pressed against the either end of the each test sample and an AC voltage was applied to the copper foil electrodes to measure the electric current.

The value of the volume resistivity of the each test sample was measured by the following method. That is, the values of the measured voltage and electric current were substituted in the following formula to determine the resistance between either electrode:

$$\text{Resistance } (\Omega) = \frac{\text{Measured voltage (V)}}{\text{Measured electric current (A)}}$$

The volume resistivity was determined by the following formula:

Volume resistivity ( $\Omega \cdot \text{cm}$ ) =

$$\frac{\text{Resistance } (\Omega) \times \text{Thickness of sheet (cm)} \times \text{Width of sheet (cm)}}{\text{Distance between either electrode (cm)}}$$

The variance in the cross direction of volume resistivity in the longitudinal direction was calculated by the following

formula through substitution of the maximum and minimum values of the determined volume resistivity:

$$\begin{aligned} \text{variance in the cross direction of} \\ \text{volume resistivity in the longitudinal direction} &= \left[ \frac{\text{maximum} \\ &\text{value of determined volume resistivity} - \\ &\text{minimum value of determined volume resistivity}}{\text{value of determined volume resistivity}} \right] \times \\ &100(\%) = (B/A) \times 100(\%) \end{aligned}$$

#### Comparative Examples 1, 2

PTFE fine powder containing conductive carbon powder (HS500, Asahi Carbon Co., Ltd.) (25 weight percent) was mixed with white oil (85 weight percent). Pressure (50 kgf/cm<sup>2</sup>) was applied to the mixture for preforming. This preformed material was inserted into the extruder shown in FIG. 5(a) with a cylinder of 130 mm in diameter and a dice outlet of 18 mm in diameter. Under the pressure of approximately 73 kgf/cm<sup>2</sup>, the material was extruded in a rod-like form.

This material was rolled through a calendering roll having 500 mm diameter at 60° C. into a sheet of 150  $\mu\text{m}$  thickness. As tensile force was applied in the cross and longitudinal directions, the sheet was sintered in a oven at 380° C. for 2 minutes.

Under various extruding and rolling conditions, the volume resistivity was measured and the states of sheets were carefully observed. The results are summarized in Table 1.

TABLE 1-1

Example	Raw material and Extruding condition	Appearance of extruded material	Calendering		Sintering condition	
			Longitudinal direction	Cross direction	Temperature (° C.)	Time (minute)
1	PTFE 75 wt % Carbon 25 wt % R.R. = 83	Tube: Diameter of Tube $\phi$ 21.5 mm Thickness of tube wall: 0.7 mm	4 times	1.4 times	360	2
2	PTFE 75 wt % Carbon 25 wt % R.R. = 48	Tube: Diameter of Tube $\phi$ 100 mm Thickness of tube wall: 0.5 mm	4 times	1.3 times	360	2
3	PTFE 75 wt % Carbon 25 wt % R.R. = 46	Tube: Diameter of Tube $\phi$ 45 mm Thickness of tube wall: 0.6 mm	4 times	1.4 times	360	2
4	PTFE 75 wt % Carbon 25 wt % R.R. = 50	Tube: Diameter of Tube $\phi$ 45 mm Thickness of tube wall: 0.55 mm	4 times	1.3 times	360	2

TABLE 1-1-continued

	Raw material and	Appearance of	Calendering		Sintering condition	
	Extruding condition		extruded material	Longitudinal direction	Cross direction	Temperature (° C.)
<u>Comparative Example</u>						
1	PTFE 75 wt % Carbon 25 wt % R.R. = 52	Rod: Diameter of Rod $\phi$ 18 mm	4 times	11 times	360	2
2	PTFE 75 wt % Carbon 25 wt % R.R. = 52	Rod: Diameter of Rod $\phi$ 18 mm	3.8 times	12 times	360	2

TABLE 1-2

State of Sheet after sintering			conductivity in the longitudinal direction: Volume	variance in the cross direction of volume resistivity in the longitudinal	Remarks
Thickness ( $\mu$ m)	Tensile strength (kg/cm <sup>2</sup> )	Width (mm)	resistivity ( $\times 10^{-1} \Omega$ - cm)	direction (%)	
<u>Example</u>					
1	110	Longitudinal direction/Cross direction = 285/140	95	2.90	5
2	85	Longitudinal direction/Cross direction = 290/145	400	2.85	5
3	100	Longitudinal direction/Cross direction = 290/143	200	2.95	5
4	140	Longitudinal direction/Cross direction = 287/142	170	2.90	5
<u>Comparative Example</u>					
1	140	Longitudinal direction/Cross direction = 250/165	170	3.30	20
2	120	Longitudinal direction/Cross direction = 250/166	200	3.30	23
Wavy edges were observed in appearance					

These experimental results demonstrate that the highly conductive PTFE sheet of the invention is sufficiently wide and has nearly uniformity in the cross direction of conductivity in the longitudinal direction, and that the invented sheet is clearly better than the wide-type sheets produced by the conventional methods.

According to this invented method, a paste of PTFE powder is extruded in a tube-like form. At least one place on the circumference of the extruded tube-like material, the material is cut open longitudinally and the resulting sheet calendered if necessary. In this way, a wide-type sheet with uniformity in the cross direction of conductivity in the longitudinal direction can be obtained.

By this invented method, wide-type PTFE sheets with uniformity in the cross direction of conductivity in the longitudinal direction are produced with high reproducibil-

ity. Therefore, these PPFE sheets can be used as a raw material for sheet-type heating elements because of their uniform exothermic properties, while they can be used as a raw material for electrodes of primary batteries, secondary batteries and fuel cells because of their water repellent properties.

The invented sheets are not less than 170 mm in width and have excellent conductivity (variance in the cross direction of volume resistivity in the longitudinal direction should be 10% or less, preferably 7% or less).

The invented manufacturing method requires only simple and small equipment (a calendering roll with small-diameter is available), thus reducing the cost because of the compactness of the equipment. Beside these advantages, this highly conductive PTFE sheet has the following excellent properties. Although the edges of the sheets produced by conventional method easily become wavy, be cracked and serrated,

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this new sheet suffers none of these defects. The edge of this new sheet forms an almost straight line and the loss of the sheet is decreased, which significantly improves the yield of the sheet.

What is claimed is:

1. A manufacturing method of a highly conductive polytetrafluoroethylene sheet, said method comprising the steps of:

admixing a paste of polytetrafluoroethylene powder with  
conductive substance, being 15-50 wt. % of the PTFE,  
and extrusion lubricant, being 10 to 60 wt. % of PTFE;  
extruding the admixture into a preform unsintered tube  
material by a RAM extruder using an extrusion pres-  
sure of 70 to 300 Kg/cm<sup>2</sup> to a thickness of 0.3 to 5 mm,  
cutting longitudinally at least one place on a circumfer-  
ence of the unsintered tube material, and  
calendering the resulting sheet  
wherein said highly conductive polytetrafluoroethylene  
sheet is not less than 170 mm in width and the variance  
of volume resistivity in the longitudinal direction is  
10% or less.

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2. A manufacturing method as defined in claim 1 further comprising the step of sintering the highly conductive polytetrafluoroethylene sheet.

3. A manufacturing method as defined in claim 1 or 2 wherein the unsintered tube extruded material has an orientation of polytetrafluoroethylene particles, at least in the internal and external surface layers, in the longitudinal direction.

4. A manufacturing method as defined in claim 1 or 2 wherein the unsintered tube extruded material has an orientation of polytetrafluoroethylene particles in the longitudinal direction.

5. A manufacturing method as defined in claim 1 or 2 wherein the sheet is extended by calendering in the longitudinal direction 1 to 10 times.

6. A manufacturing method as defined in claim 1 or 2 wherein the sheet is extended by calendering along the width 1 to 3 times.

\* \* \* \* \*



US005227105A

**United States Patent** [19]

Eucker et al.

[11] Patent Number: **5,227,105**[45] Date of Patent: **Jul. 13, 1993**[54] **PROCESS FOR MANUFACTURING CERAMIC TUBES**[75] Inventors: **James L. Eucker**, Fairview Park;  
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both of Ohio; **Irving B. Ruppel, Jr.**,  
Kenmore, N.Y.[73] Assignee: **The Carborundum Company**, Niagara  
Falls, N.Y.[21] Appl. No.: **524,264**[22] Filed: **Jul. 9, 1990****Related U.S. Application Data**[62] Division of Ser. No. 322,482, Mar. 10, 1989, Pat. No.  
5,057,001.[51] Int. Cl.<sup>5</sup> ..... **C04B 35/64**[52] U.S. Cl. .... **264/57; 264/63;**  
**264/150; 264/102; 264/177.11; 264/211.11**[58] Field of Search ..... **264/57, 150, 63, 211.11,**  
**264/177.11, 102**[56] **References Cited****U.S. PATENT DOCUMENTS**

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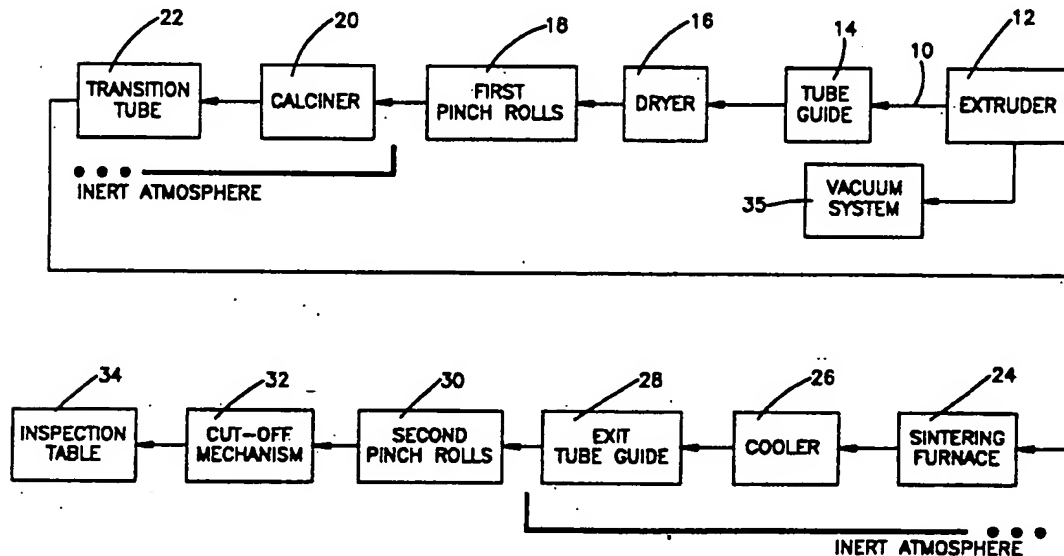
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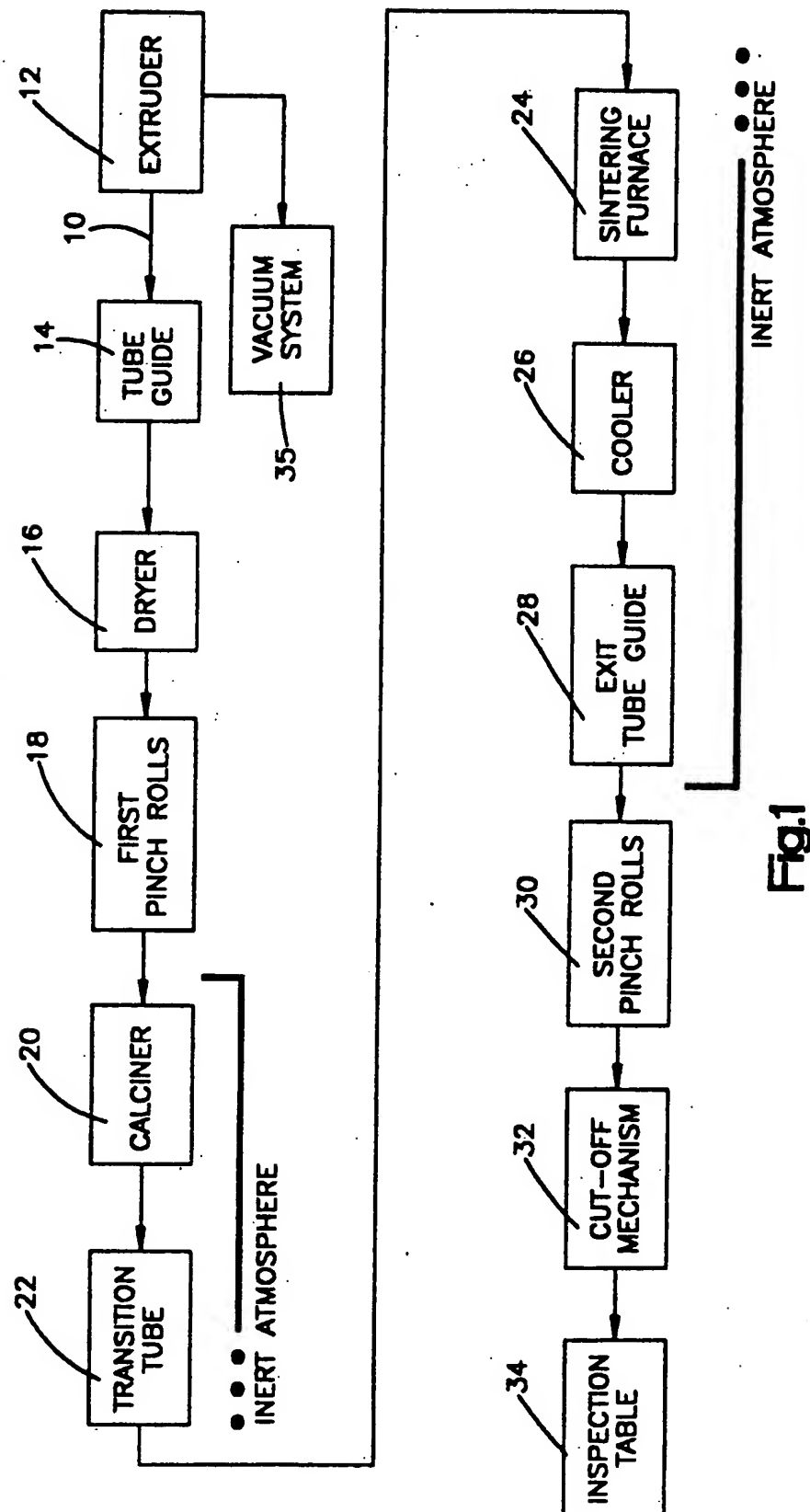
*Primary Examiner*—James Derrington*Attorney, Agent, or Firm*—Fay, Sharpe, Beall, Fagan,  
Minnich & McKee

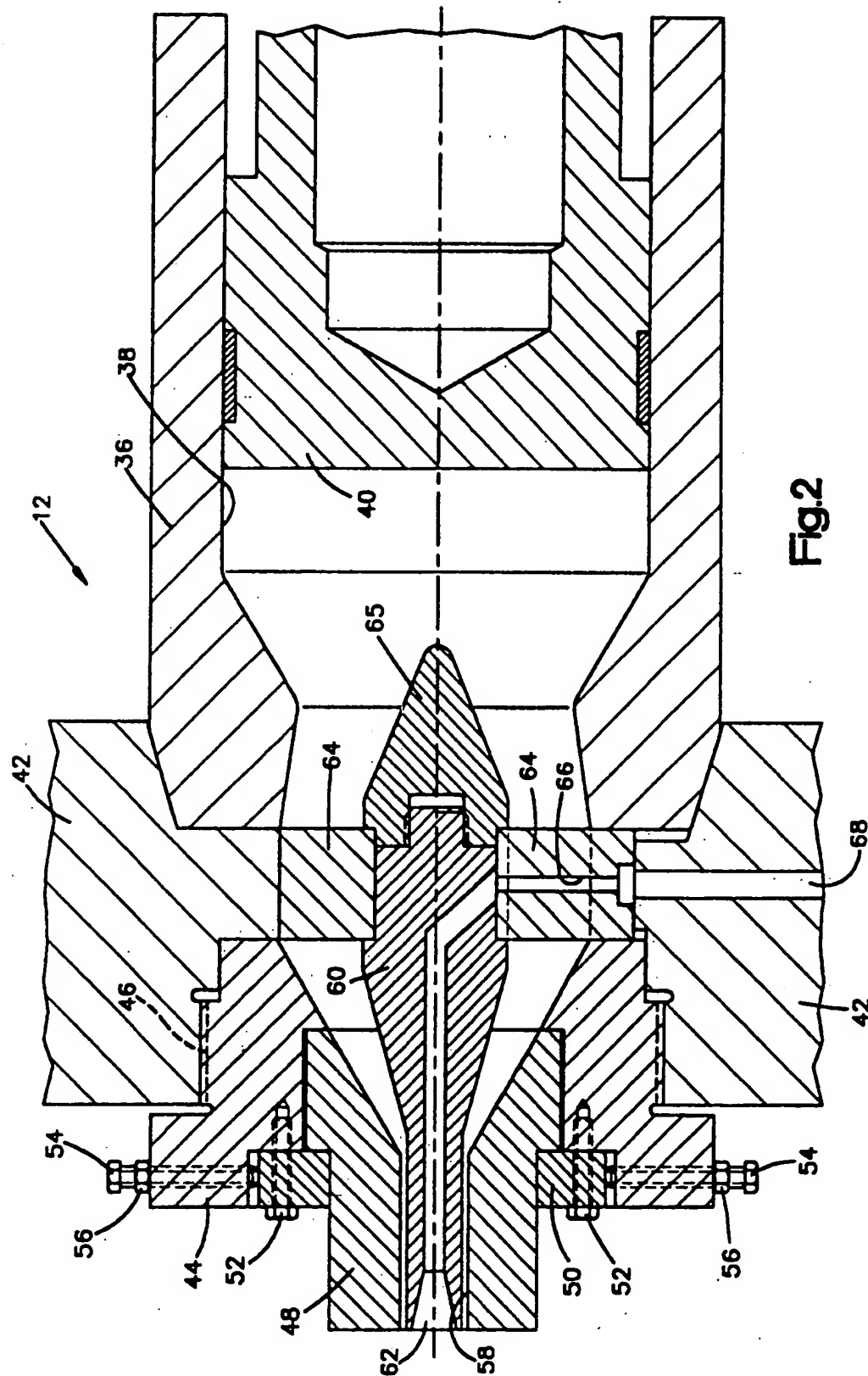
## [57]

**ABSTRACT**

Ceramic tubes are manufactured from a mixture that includes ceramic powder. The mixture is extruded through a die to form a tube. The tube is passed through an open-ended dryer, calciner, transition zone, sintering furnace, and cooler. Thereafter, the tube is cut to the desired length (which may be very long). The quality of the tube is enhanced by applying a vacuum to the mixture prior to extrusion. For tubes made of non-oxide ceramics, an inert atmosphere is maintained both inside and outside the tube in all sections of the equipment that operate above 200° C. A controlled tension is applied to the tube by means of first pinch rolls disposed downstream of the dryer and second pinch rolls disposed downstream of the cooler.

**34 Claims, 17 Drawing Sheets**





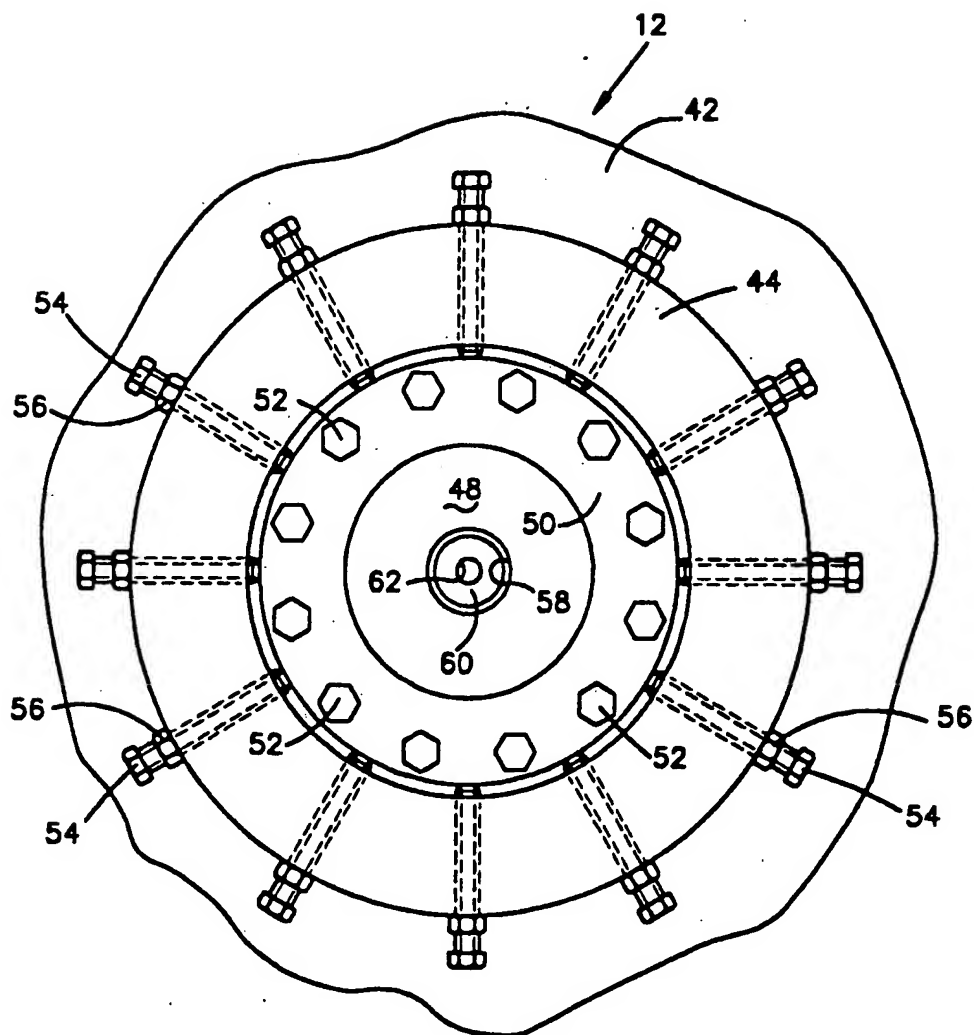
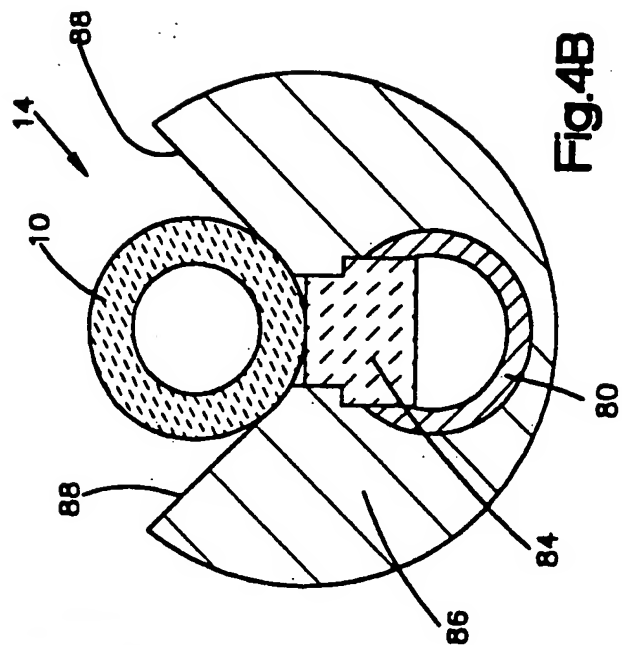
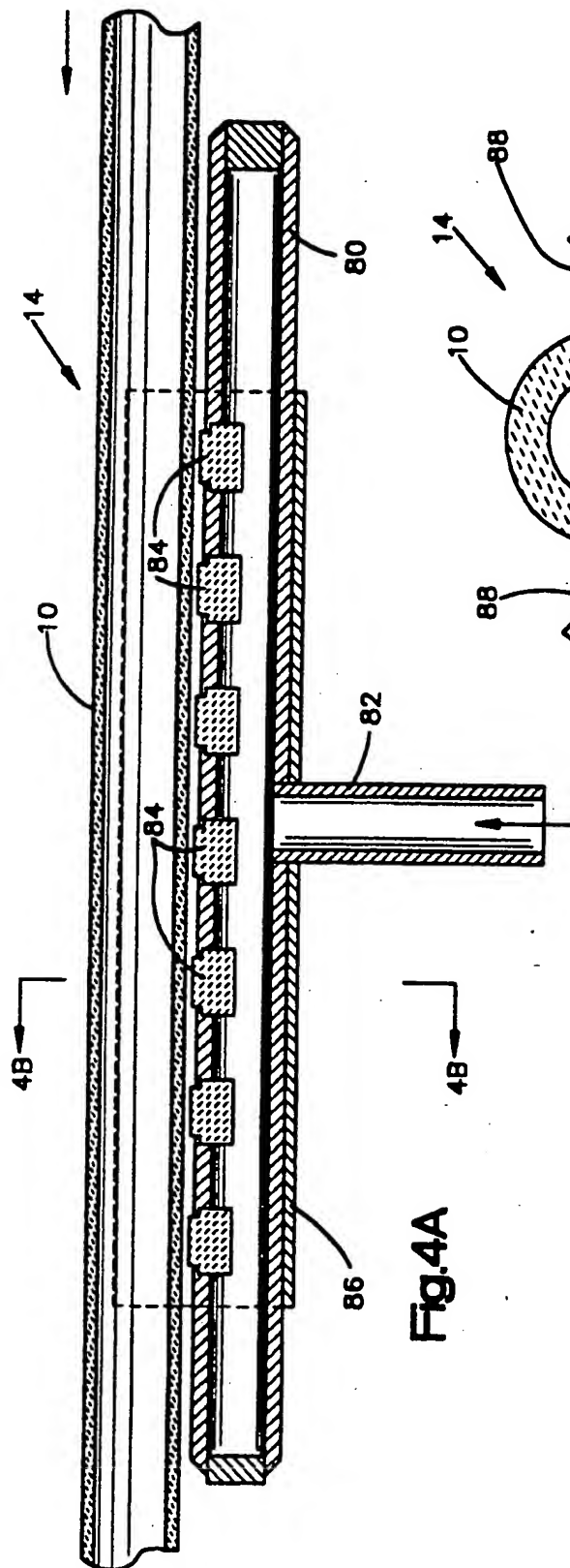


Fig.3





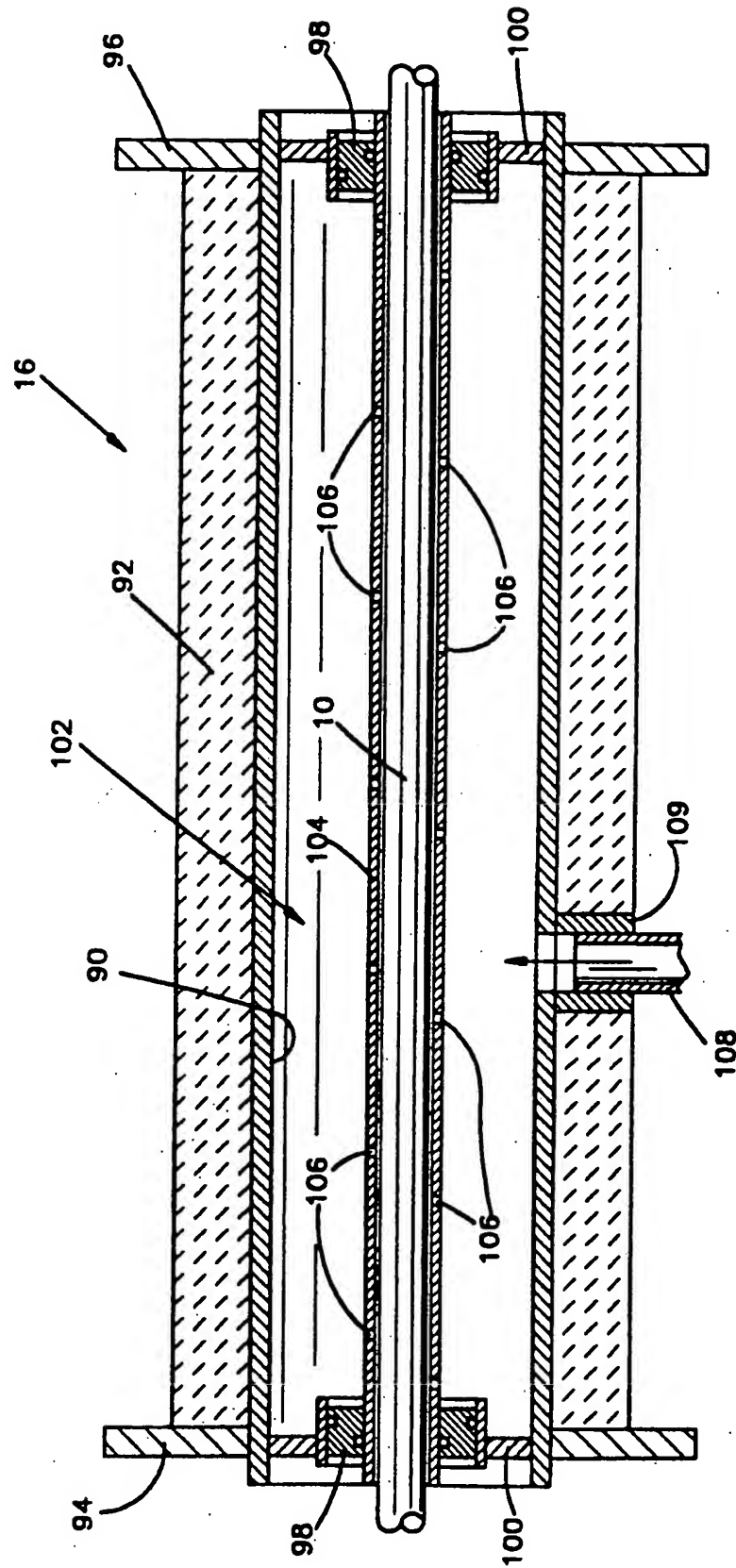
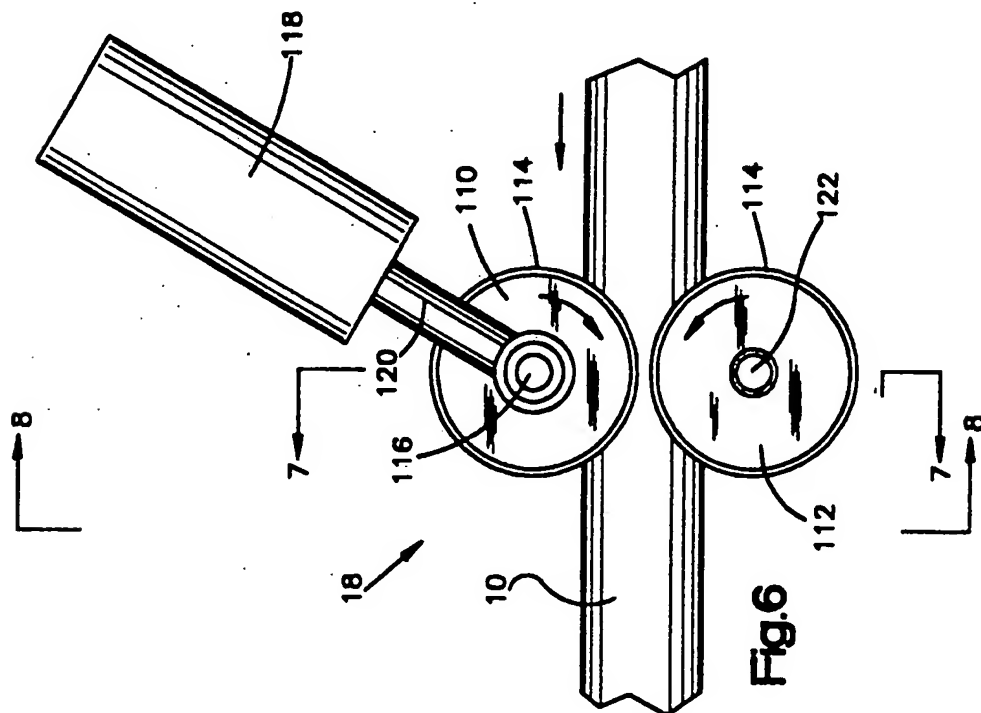
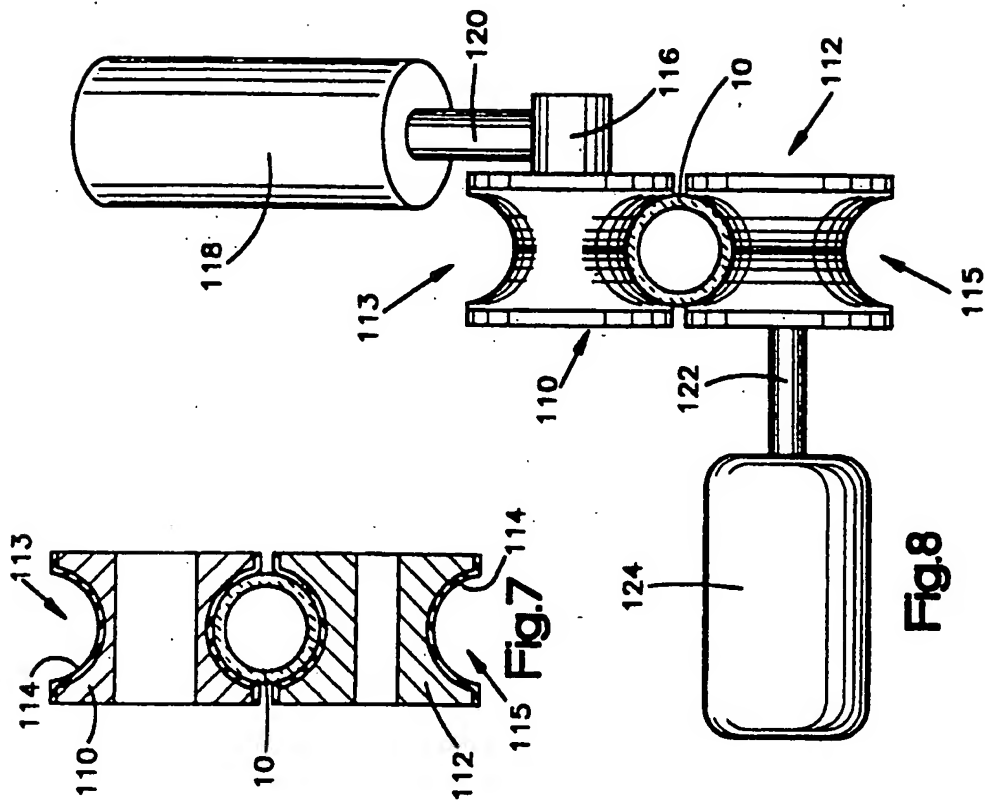
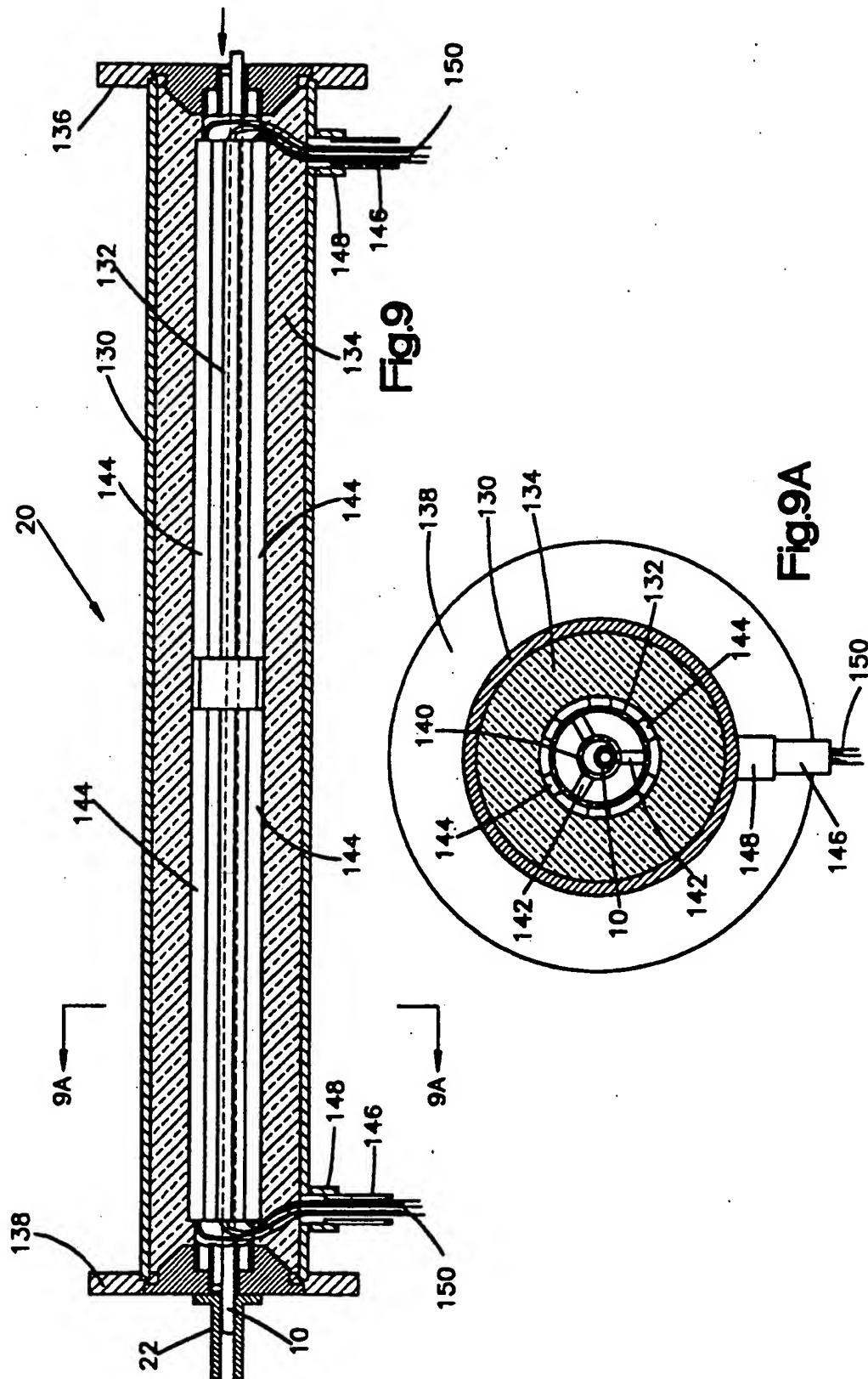


Fig.5





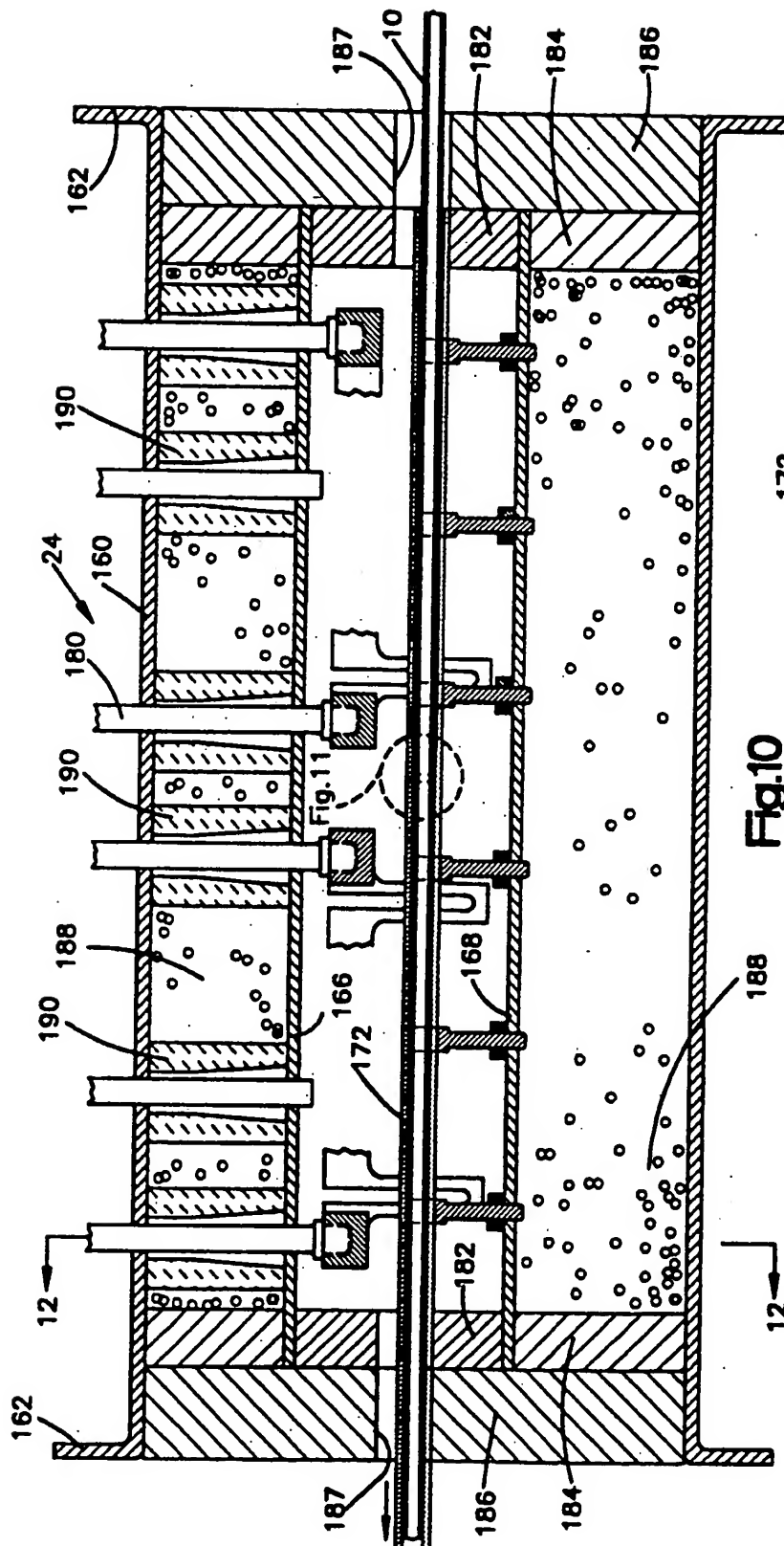


Fig. 10

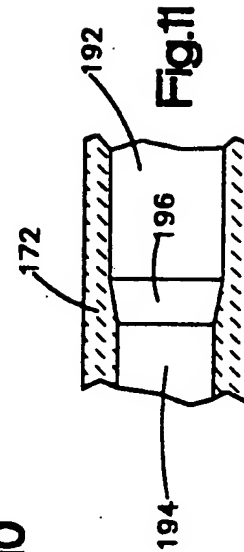


Fig. 11

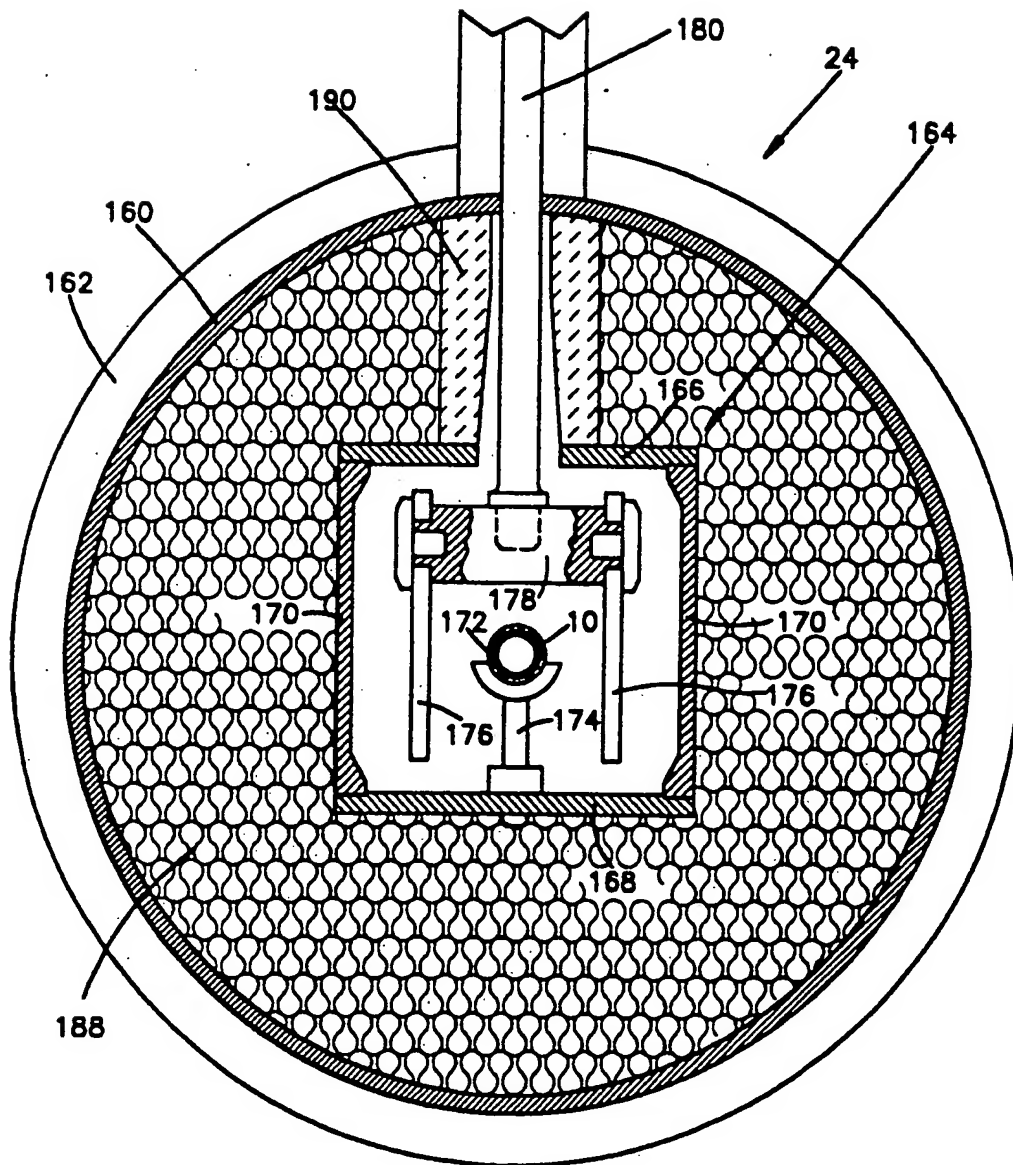
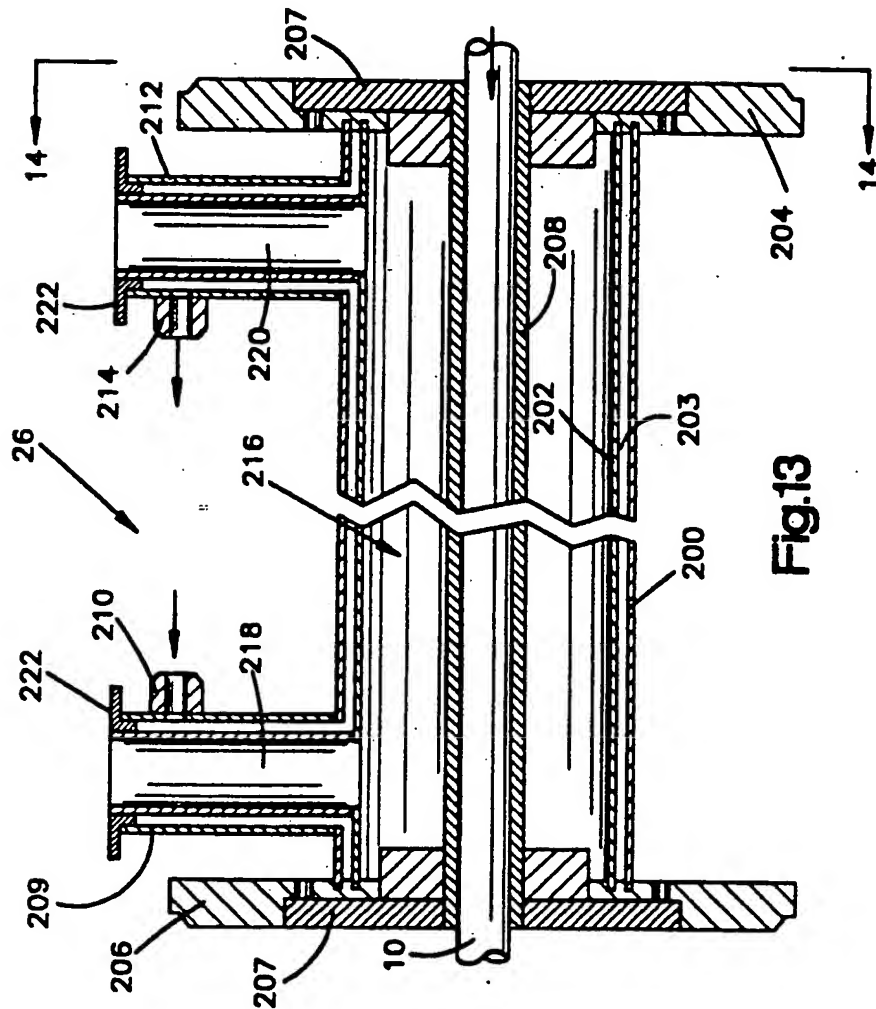
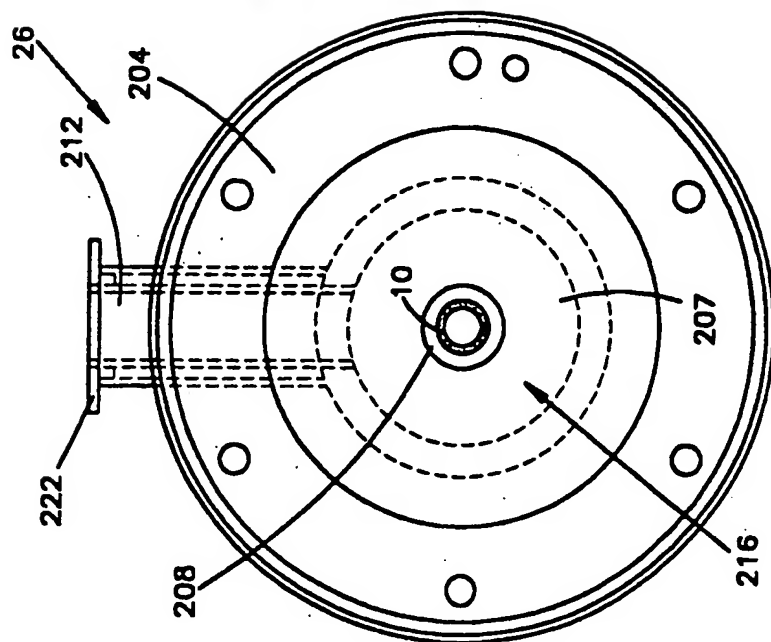


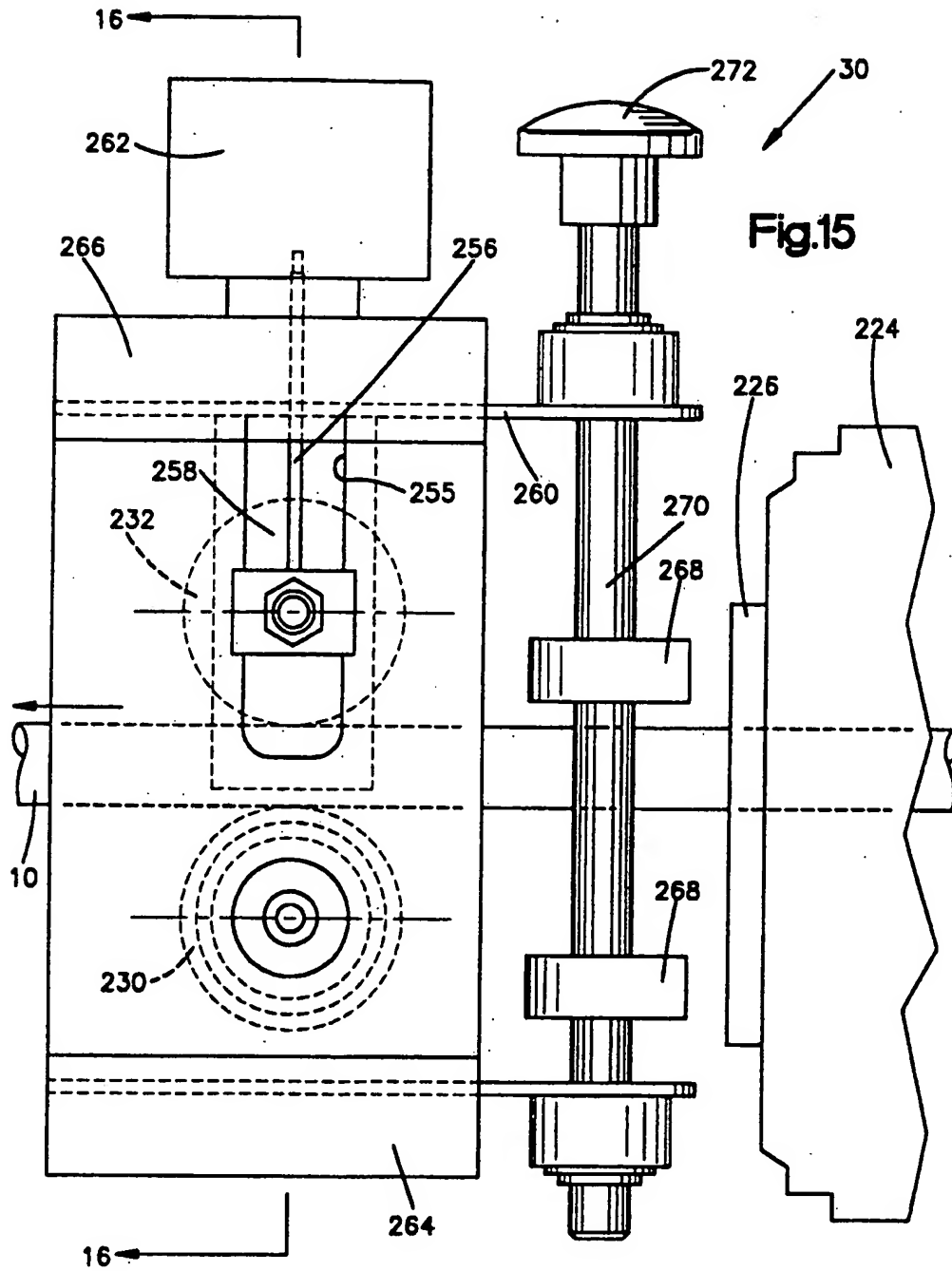
Fig.12



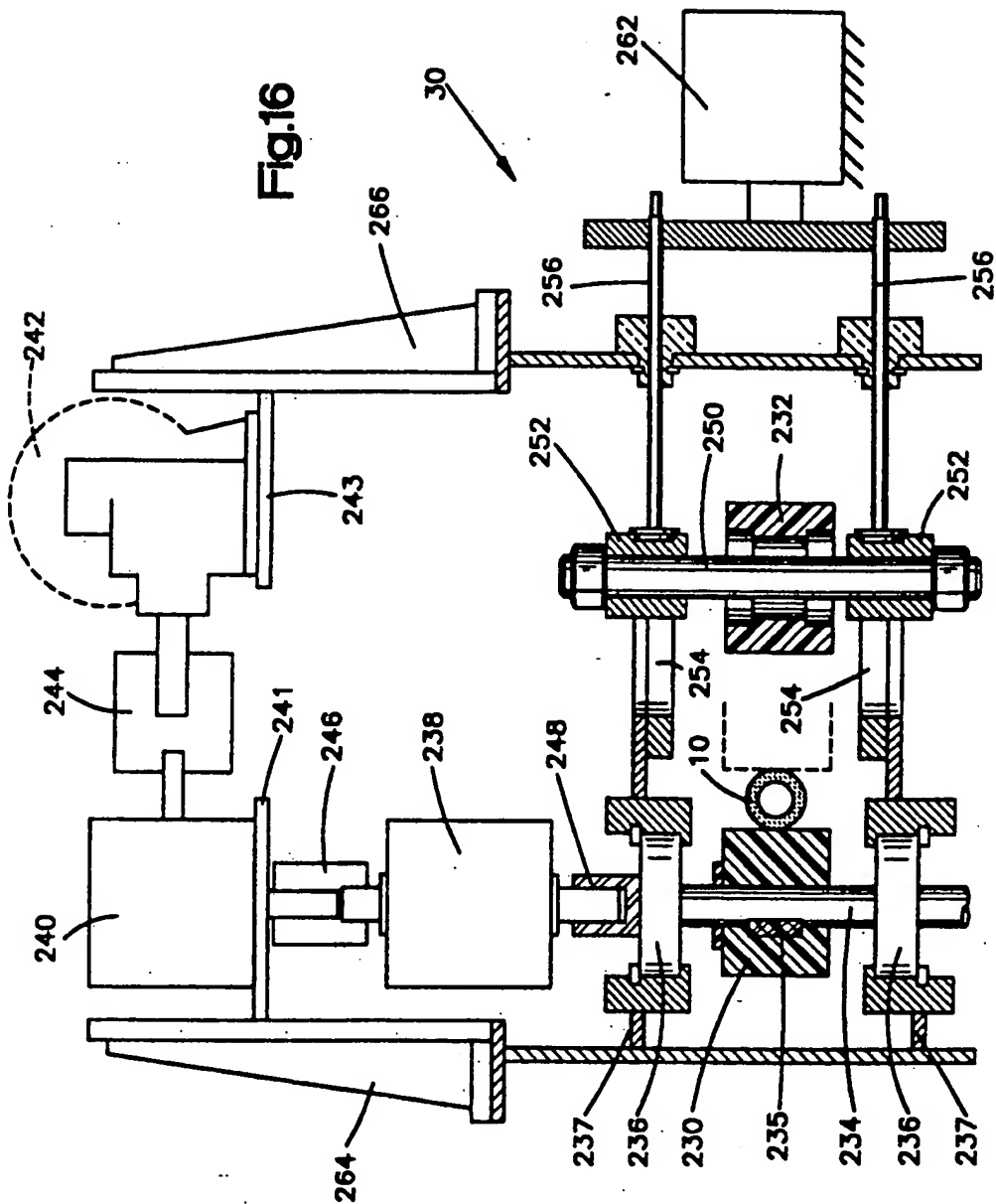
**Fig. 13**



**Fig.14**







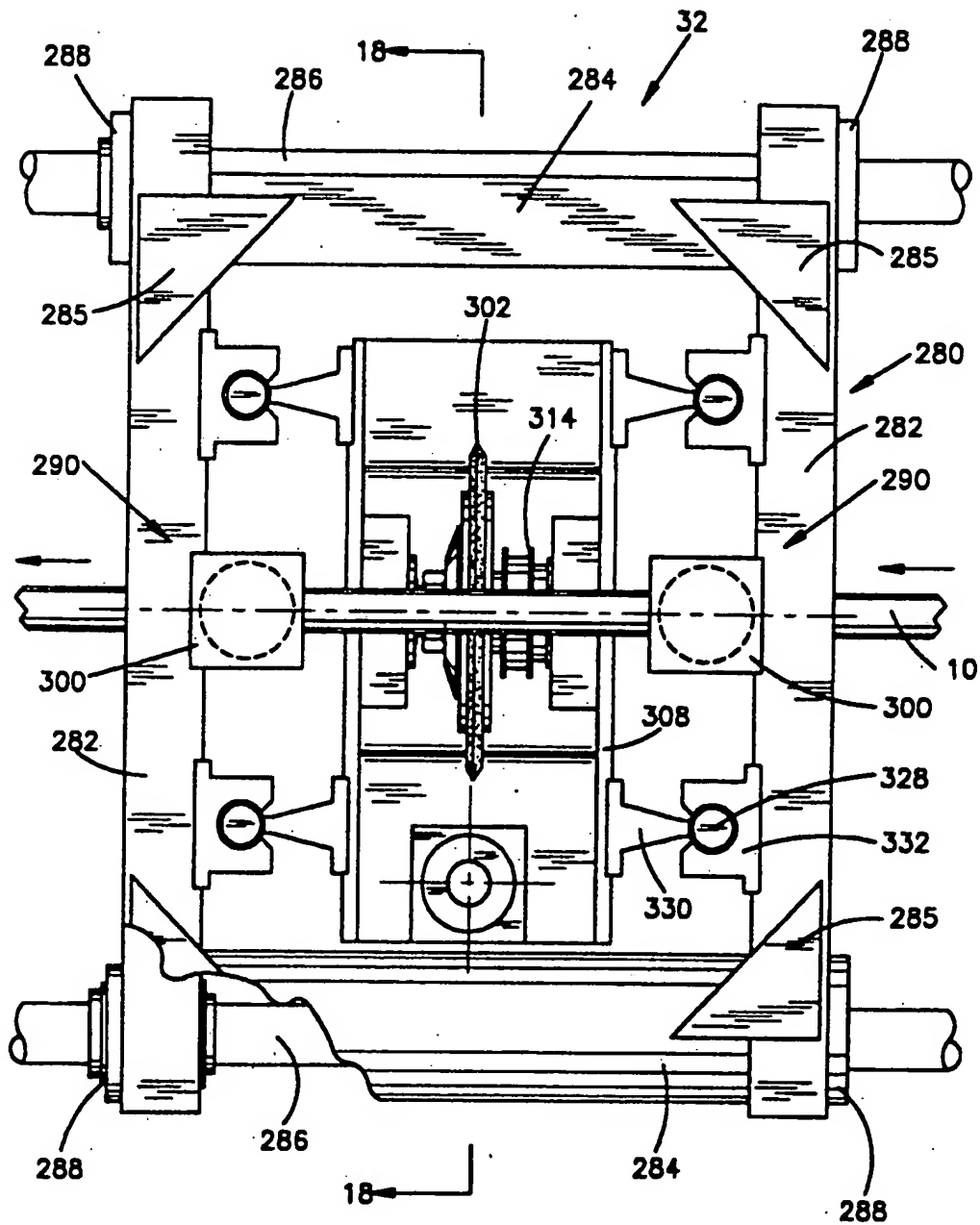


Fig.17

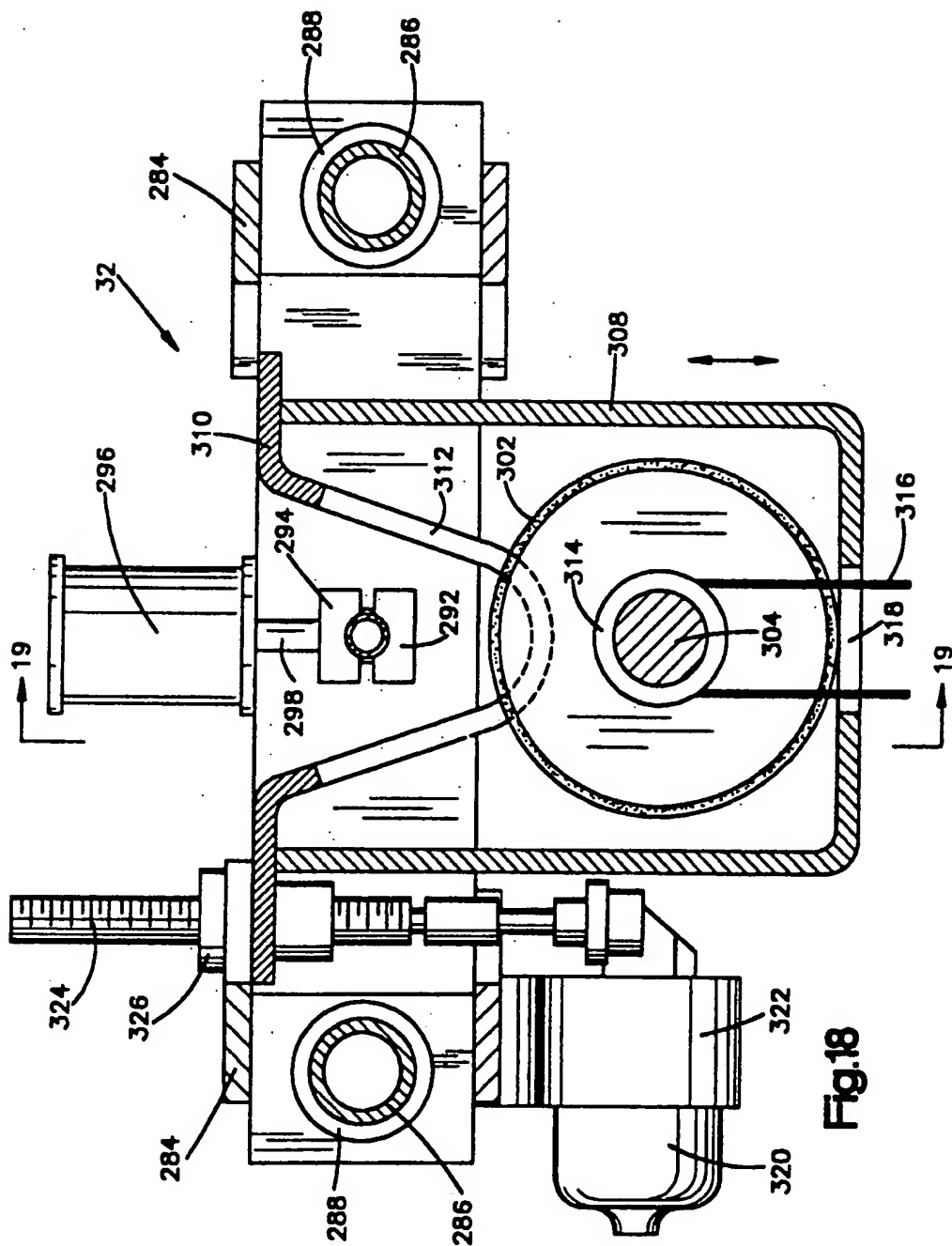
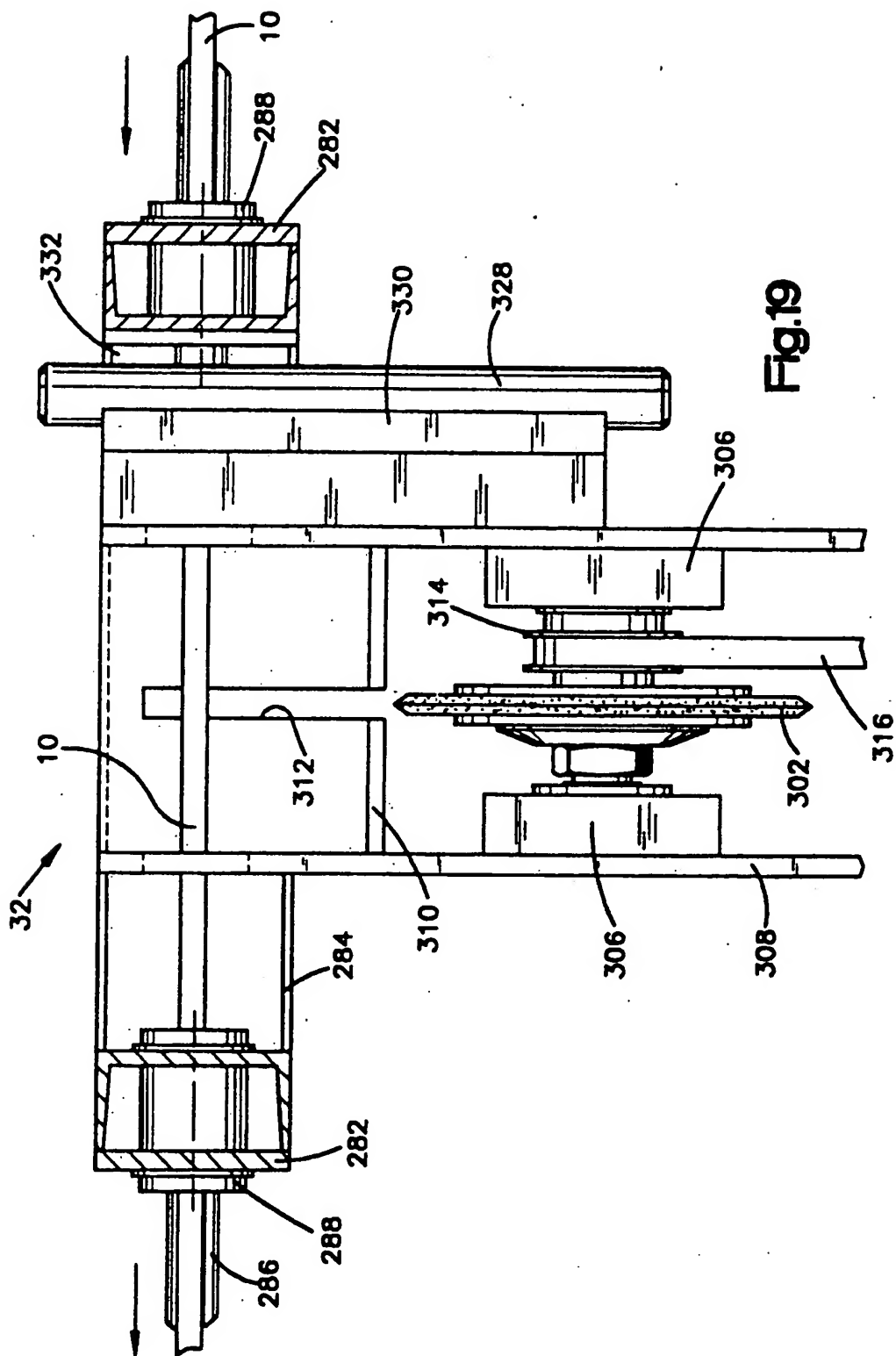


Fig.18



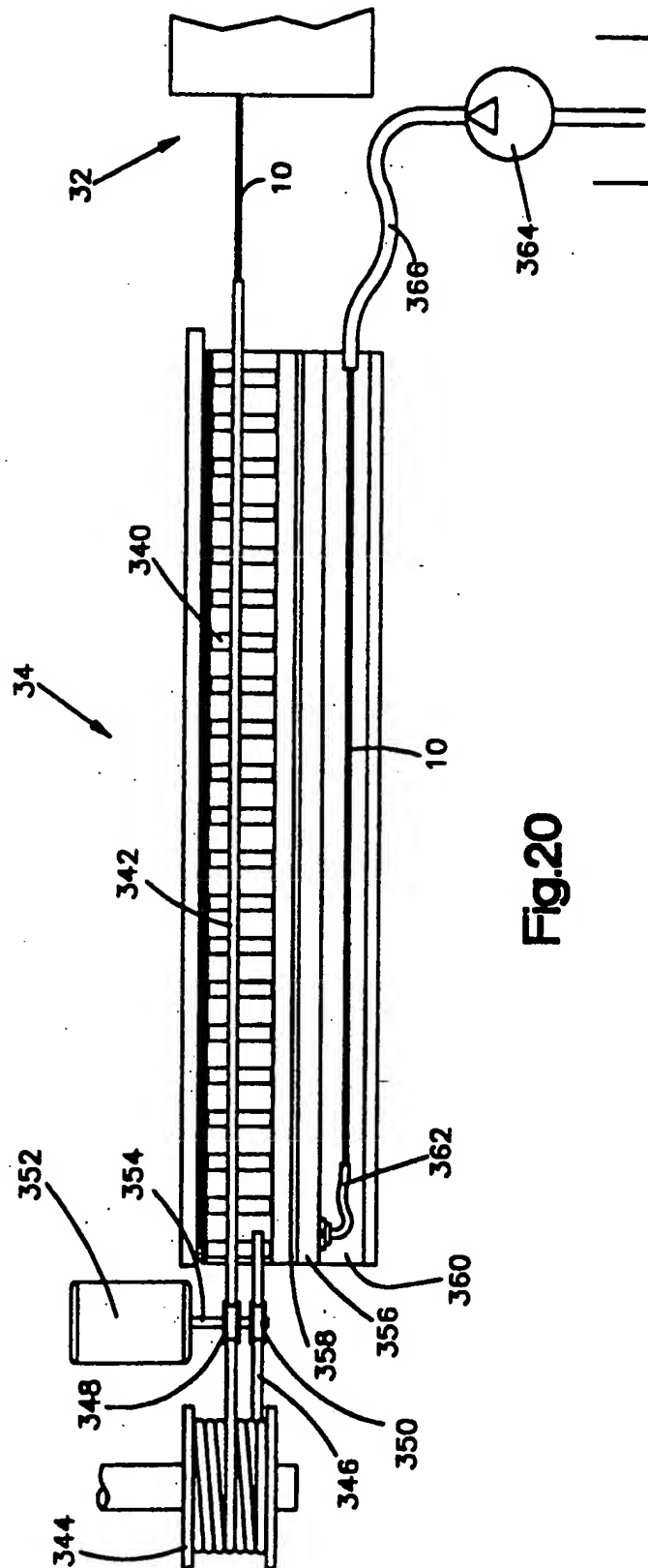
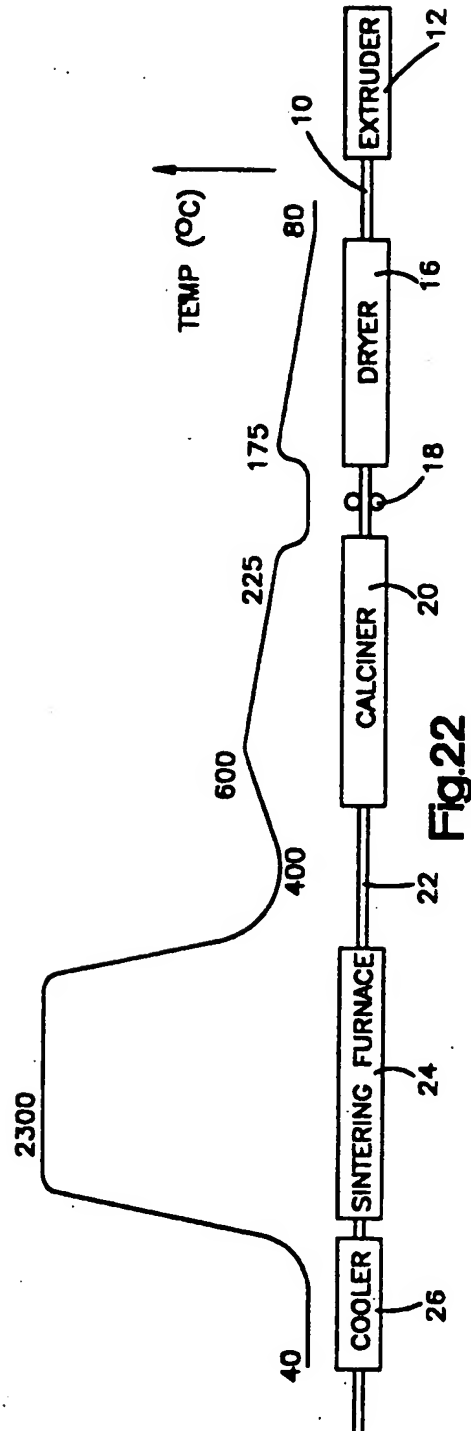
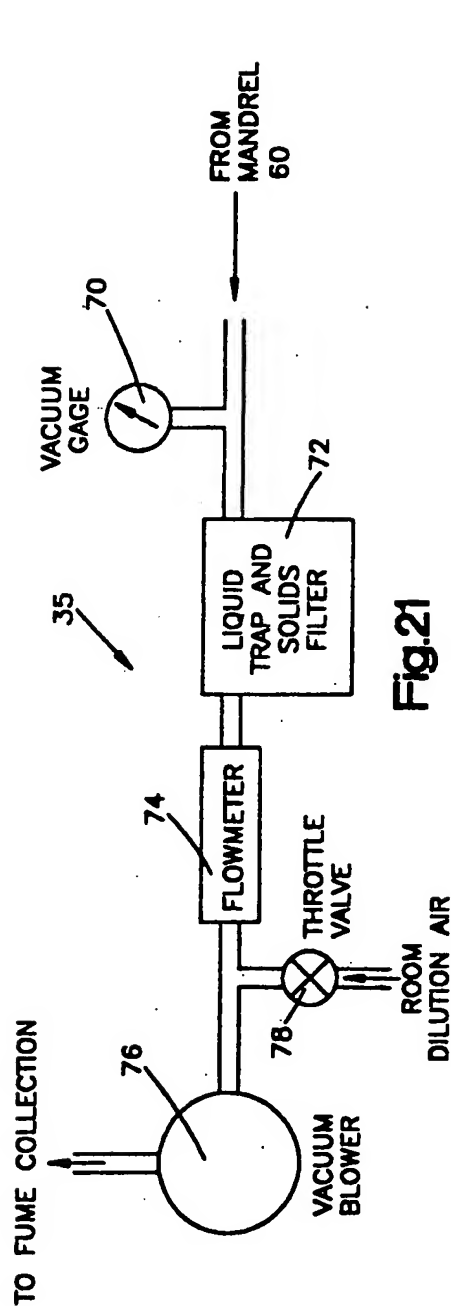


Fig. 20



## PROCESS FOR MANUFACTURING CERAMIC TUBES

This application is a division of application Ser. No. 07/322,482, filed Mar. 10, 1989, now U.S. Pat. No. 5,057,001.

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The invention relates to the manufacture of ceramic tubes and, more particularly, to a method and apparatus for manufacturing ceramic tubes on a substantially continuous basis.

#### 2. Description of the Prior Art

Ceramic tubes are used in heat exchangers where corrosive liquids or gases are handled, in high-temperature applications such as recuperators, in certain types of electrolytic cells, and in various other applications. Ceramic tubes currently are manufactured from ceramic materials such as sintered alpha silicon carbide, sintered aluminum oxide, sintered zirconia, and various others. Ceramic tubes are manufactured in a variety of diameters and wall thicknesses, and some currently are manufactured with longitudinal internal fins for enhanced surface area.

Ceramic tubes presently are manufactured by a so-called batch process wherein a series of separate steps are performed upon individual tubes. Unfortunately, batch-produced tubes cannot be manufactured in lengths any longer than approximately 14 feet due to various equipment limitations and to processing limitations including the cumulative length shrinkage. If long tubes (over about 14 feet) are being manufactured, the equipment needed to manufacture the tubes becomes very expensive. Also, it is possible to have differential properties from one end of the tube to the other as the length of the tube is increased. An additional drawback of the batch process is that damage can occur to tubes in process because the tubes must be handled frequently, that is, they must be moved from station-to-station during the manufacturing process. Additional drawbacks associated with batch-manufactured ceramic tubes include a long manufacturing time, the inability to rapidly feed back quality control information from finished tubes to tubes being processed, and a lack of optimum product quality.

Patents disclosing various batch processes for the manufacture of ceramic tubes include the patent to Jones, U.S. Pat. No. 3,950,463, and the patent to Dias, et al., U.S. Pat. No. 4,265,843. Jones discloses the production of beta alumina ceramic tubes wherein tubes of a fixed length, for example 18 inches, are passed at a uniform rate through an electric inductive furnace of open-ended tubular form. The temperature of the tube is raised within a short zone into the range of 1600°-1900° C. so that the tube is rapidly sintered, and thereafter is rapidly cooled. The patent to Dias, et al. similarly operates on tubes of fixed length, for example 20 centimeters. Dias, et al. disclose contacting a fixed length carbon-containing preform with elemental silicon powder at high temperature to transform at least a major part of the carbon to silicon carbide. This is known as reaction bonding, and is considered different from sintering by those skilled in the field of ceramics. Not only do the Jones and Dias et al. manufacturing processes suffer from the drawbacks of batch manufac-

turing processes, but they also are limited to relatively short lengths of tubes.

Other batch processes are known that are suitable for the manufacture of ceramic tubes, and the use of a variety of materials in such processes also is known. For example, U.S. Pat. No. 4,124,667; U.S. Pat. No. 4,179,299; U.S. Pat. No. 4,312,954; and U.S. Pat. No. 4,346,049, all issued to Coppola, et al., the disclosures of which are incorporated herein by reference, disclose sintered alpha silicon carbide ceramic bodies that can be injection molded on a batch basis. The ceramic bodies are manufactured from a mixture including silicon carbide, a carbon source, a boron source, a temporary binder, and a solvent.

The patent to Storm, U.S. Pat. No. 4,207,226 discloses a ceramic composition suited for injection molding and sintering, which composition includes, among other constituents, minor amounts of organo-titanates which materially reduce the viscosity of the composition. The patents to Ohnsorg, U.S. Pat. No. 4,144,207 and U.S. Pat. No. 4,233,256, disclose a composition and process for injection molding ceramic materials wherein a particular ceramic mixture includes, among other constituents, a combination of thermoplastic resin and oils or waxes. Although the Storm and Ohnsorg patents disclose ceramic compositions having desirable properties, they fail to teach or suggest any technique for overcoming the drawbacks of batch manufacturing processes.

Desirably, it would be possible to manufacture ceramic tubes more or less continuously so that tubes of essentially endless length could be manufactured and then cut to whatever length (for example, up to 60 feet or more) may be desired. It also would be advantageous to manufacture ceramic tubes by reducing handling damage, by providing a high degree of symmetry to the processing of the tubes at each stage, and by permitting rapid feedback of final product quality data to the early stages of the manufacturing process.

### SUMMARY OF THE INVENTION

The present invention overcomes the foregoing drawbacks of the prior art and provides a new and improved method and apparatus for the manufacture of ceramic tubes. The present invention involves the manufacture of ceramic tubes from a mixture that includes ceramic powder. In the preferred embodiment, the ceramic powder is alpha silicon carbide that is mixed with a carbon source and a boron source to form a premix. A water-soluble plasticizer, preferably methylcellulose ether, is added to the premix. A solvent such as water is added as needed to control the viscosity to form an extrudable mixture. The mixture is compacted and evacuated and placed in an extruder. The compacted and evacuated mixture then is extruded through a die containing a central mandrel to produce a tube having a desired cross-sectional configuration and wall thickness. While continuously extruding the mixture, the tube is passed through an open-ended dryer, calciner, transition zone, sintering furnace, and cooler. After passing through the cooler, the tube is cut to length.

The extrusion mixture first is mixed in a high-intensity mixer and then is formed into a solid-cylinder "billet" in a separate press, with much of the air in the billet being evacuated by applying a vacuum to the billet-making press. The billet then is loaded into the extruder and again a vacuum is applied to remove air from the

extrusion chamber. During long runs, the entire is stopped briefly (1-2 minutes) for adding a new billet when required. Alternately, it is contemplated that a screw drive extruder may be used which would eliminate the need to stop the entire line to add new starting material. In this alternative mode, it is contemplated that the extrusion mixture would not have to be compacted; evacuation could be accomplished by applying a vacuum to the input means of the screw drive extruder.

The tube preferably is extruded in a horizontal plane and preferably is supported after extrusion and before drying on a cushion of air. The dryer is operated at about 175° C. air inlet temperature in order to remove water. The calciner is operated at about 550°-600° C. at the exit end in order to vaporize the volatiles. The sintering furnace is operated at about 2250°-2300° C. (depending on the composition of the tube, among other factors) in order to sinter the ceramic powder. The transition zone between the calciner and the sintering furnace isolates the volatiles released in the calciner from the sintering furnace. These volatiles are flushed upstream by flowing an inert atmosphere on both the inside and outside of the tube. An inert atmosphere must be maintained within all parts of the line operating above about 200° C.

Tube straightness is achieved primarily through the use of a series of closely fitting guide tubes from the calciner through the cooling section, with the centerlines of the guide tubes being accurately aligned with one another. The inside diameter of these guide tubes is reduced part way through the sintering furnace to conform to the diameter reduction which occurs during sintering. Proper line tension through the sintering section also is helpful in maintaining straightness. Tension is applied to the tube during the extrusion process by means of first pinch rolls disposed downstream of the dryer and second pinch rolls disposed downstream of the cooler. By appropriately controlling the pinch rolls, and the slippage thereof in respect to the tube, the finished tube will be straight, and it will have a uniform wall thickness and outside diameter.

The tube is cut to length by means of a flying cut-off machine disposed adjacent the tube downstream of the cooler. A clamp grips the tube and moves the cut-off machine together with the tube while a diamond abrasive-type cut-off wheel severs the tube. The severed tube is directed onto a run-out table for subsequent inspection and packaging operations. After the tube has been cut, a long hose equipped with a fitting is connected to the end of the tube being produced, which hose is used to introduce a controlled flow of inert gas into the interior of the tube. The inert gas is passed upstream within the tube and is withdrawn through a vacuum port in the mandrel, thus removing water and volatiles from inside the tube and preventing them from entering the sintering zone. The term "inert" as used herein means that the gas, such as nitrogen or argon, does not react substantially with the tube material at any point in the entire line.

As is apparent from the foregoing description, the invention enables extremely long ceramic tubes to be produced on a more or less continuous basis. The tubes can have a wide variety of diameters and wall thicknesses. Tubes having internal fins also may be produced. The present invention minimizes or eliminates damage from frequent tube handling, improves processing (heat transfer and mass transfer) symmetry, permits rapid

feedback as part of the manufacturing process, and avoids the high capital cost of conventional tube manufacturing equipment.

The foregoing features and advantages will be apparent from reviewing the following description and claims, taken in conjunction with the accompanying drawings.

#### DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow chart showing equipment used to manufacture ceramic tubes;

FIG. 2 is a cross-sectional view of an extruder used as part of the invention, including a die and a mandrel that are used to form tubes;

FIG. 3 is an end view of the extruder of FIG. 2, taken from the left as viewed in FIG. 2;

FIG. 4A is a cross-sectional view of a tube guide used as part of the invention;

FIG. 4B is a cross-sectional view of the tube guide of FIG. 4A, taken along a plane indicated by line 4B-4B in FIG. 4A;

FIG. 5 is a cross-sectional view of a dryer used as part of the invention;

FIG. 6 is a schematic, side elevational view of first pinch rolls used as part of the invention;

FIG. 7 is a cross-sectional view of the pinch rolls taken along a plane indicated by line 7-7 in FIG. 6;

FIG. 8 is an end elevational view of the pinch rolls taken along a plane indicated by line 8-8 in FIG. 6;

FIG. 9 is a cross-sectional view of a calciner used as part of the invention;

FIG. 9A is a cross-sectional view of the calciner of FIG. 9, taken along a plane indicated by line 9A-9A in FIG. 9;

FIG. 10 is a cross-sectional view of a sintering furnace used as part of the invention;

FIG. 11 is an enlarged view of a portion of the sintering furnace of FIG. 10, showing a portion of a tube guide used as part of the invention;

FIG. 12 is a cross-sectional view of the sintering furnace of FIG. 10, taken along a plane indicated by line 12-12 in FIG. 10;

FIG. 13 is a cross-sectional view of a cooler used as part of the invention;

FIG. 14 is an end elevational view of the cooler of FIG. 13;

FIG. 15 is a top plan view, with certain parts shown in phantom, of second pinch rolls used as part of the invention;

FIG. 16 is a cross-sectional view of the second pinch rolls taken along a plane indicated by line 16-16 in FIG. 15;

FIG. 17 is a top plan view of a tube cut-off mechanism used as part of the invention;

FIG. 18 is a cross-sectional view of the cut-off mechanism of FIG. 17 taken along a plane indicated by line 18-18 in FIG. 17;

FIG. 19 is a cross-sectional view of a portion of the cut-off mechanism of FIG. 17 taken along a plane indicated by line 19-19 in FIG. 18;

FIG. 20 is a schematic top plan view of an inspection table used as part of the invention;

FIG. 21 is a schematic representation of a vacuum system used as part of the invention; and

FIG. 22 is a graph showing the temperature of tubes manufactured according to the invention as a function of the location of the tubes during the manufacturing process.



## DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to FIG. 1, apparatus suitable for the manufacture of ceramic tubes 10 is indicated schematically. The tube-making apparatus includes an extruder 12, a tube guide 14, a dryer 16, first pinch rolls 18, a calciner 20, a transition tube 22, a sintering furnace 24, a cooler 26, an exit tube guide 28, second pinch rolls 30, a cut-off mechanism 32, an inspection table 34, and a vacuum system 35. The tube-making apparatus will be described by its individual components, including the composition of the tubes 10.

### THE TUBES 10

The term "tubes" as used herein primarily refers to elongate cylindrical shapes. The invention can be used to produce other shapes such as solid rods of circular or non-circular cross-section, hollow or solid shapes with external fins, and hollow shapes of circular or non-circular cross-section with internal fins and/or external fins. The invention encompasses all such shapes by the use of the word "tubes".

The sintered alpha silicon carbide tubes 10 are hard, durable, gas-impervious cylinders that can withstand the corrosive and erosive effects of almost any gaseous or liquid material, including high temperature sulfuric acid. Although the tubes in finished form are relatively brittle, they otherwise possess excellent structural integrity and will withstand high temperatures, high pressures, and chemical attack.

The tubes are made from a ceramic material, preferably alpha silicon carbide. Other types of ceramic materials that can be used include aluminum oxide and zirconia. The tubes 10 are sintered, and thus the ceramic powder must be mixed with other ingredients that will enable the powder to be extruded and thereafter sintered. Tubes having a controlled wall porosity also may be manufactured using a pore-forming additive such as carbon. The additive is added to the extrusion mixture and later removed from the finished tubes.

The tubes 10 are manufactured by first making a premix. The premix includes a suitable ceramic powder such as alpha silicon carbide, a suitable sintering aid (boron source) such as boron carbide ( $B_4C$ ), and one or more organic binders, preferably phenolic. The binder also acts as a carbon source to aid in the sintering of the ceramic powder. The premix is a fine, powdery, homogeneous mixture that does not require any special handling or storage precautions. Reference is made to U.S. Pat. No. 4,179,299 and U.S. Pat. No. 4,312,954 for teachings of particularly desirable alpha silicon carbide premix composition.

A plasticizer is added to the premix to aid in the extrusion process. A preferred plasticizer is methylcellulose ether. Methylcellulose ether is commercially available under the trademark METHOCEL.

The premix-plasticizer mixture is blended with a solvent such as water until a desired viscosity for extrusion is attained. A typical mixture composition would be about 79.6% by weight of silicon carbide premix, 2.1% by weight of A-4M METHOCEL methylcellulose ether, and 18.1% by weight of deionized water. The amount of water in the initial mixture typically is within the range of about 17.0-20.0% by weight. It has been found that if the water is added in the form of ice, or if the mixture is cooled during mixing, then both the green tubes and the sintered tubes have higher density.

The mixture is mixed in a high-intensity mixer and then is formed into a solid-cylinder "billet" in a separate press, with much of the air in the billet being evacuated by applying a vacuum to the billet-making press. A typical billet weights at least 10 pounds and one or two billets usually are charged into the extruder 12 at one time.

### THE EXTRUDER 12

Referring to FIGS. 2 and 3, the extruder 12 includes a container 36 having a longitudinally extending bore 38. A ram 40 is disposed in the upstream portion of the bore 38. The ram 40 is connected to a DC drive motor and gearbox plus screwjack (not shown) which drives the ram 40 at a very slow and accurate adjustable speed, with tachometer feedback.

The container 36 is connected to a casing 42. An adapter 44 is secured to the forward-facing portion of the casing 42 by means of threads indicated at 46. A die 48 is secured to the forwardmost portion of the adapter 44 by means of a ring 50 and bolts 52. A plurality of radially extending bolts 54 extend through the adapter 44 and into engagement with the outer diameter of the ring 50. The bolts 54 are locked in place relative to the adapter 44 by means of locknuts 56.

The die 48 includes a longitudinally extending bore 58 of a desired cross-section. As illustrated, the cross-section is circular, but it could be non-circular if desired, as noted earlier. An elongate mandrel 60 having a hollow interior 62 is disposed within the bore 58 and is secured in place there by means of radially extending supports 64. A rounded cone 65 is threaded to the mandrel 60 and securely attaches the mandrel 60 to the supports 64. One of the supports 64 includes a passage 66 which communicates with the interior 62 of the mandrel 60 and with a passage 68 formed in the casing 42. If a tube 10 having internal fins is desired, the inverse of the fins is incorporated into the mandrel geometry.

Referring to FIG. 21, the passage 68 is connected to the vacuum system 35. The vacuum system 35 includes a vacuum gauge 70, a liquid and solids trap 72, a flowmeter 74, and a vacuum blower 76. A throttle valve 78 enables ambient air to be used to dilute the air being drawn from the mandrel 60, so that the blower 76 will receive enough total volume of air for proper cooling of the blower 76.

As will be apparent from an examination of FIGS. 2 and 3, the spacing between the bore 58 and the mandrel 60 determines the wall thickness of the tube 10. The die 48 can be adjusted relative to the mandrel 60 in order to achieve excellent concentricity and, hence, uniform wall thickness in the extruded tube 10. The adjustment is made by appropriately tightening or loosening the bolts 54 which bear upon the ring 50. Through trial and error adjustment of the bolts 54, the die 48 eventually will be centered relative to the mandrel 60. The locknuts 56 then can be tightened to be sure that the adjustment will remain.

### THE TUBE GUIDE 14

Referring to FIGS. 4A and 4B, the tube guide 14 includes a longitudinally extending tube 80 disposed immediately downstream of the die 48. A conduit 82 is connected to the tube 80 for supplying air under pressure from a source (not shown) into the tube 80. A plurality of porous plugs 84 extend through openings formed in the upper surface of the tube 80. The plugs 84

enable air under pressure to be diffused therethrough so as to form a cushion upon which the tube 10 can be supported. The tube 80 is surrounded by a longitudinally extending trough 86 having diverging, straight-sided sidewalls 88. The sidewalls 88 diverge at an angle of approximately 90 degrees.

The tube guide 14 supports the newly extruded tube 10 and prevents it from sagging. The air diffused through the plugs 84 provides a cushion of air upon which the newly extruded tube 10 can be supported. In addition to preventing the tube 10 from sagging, the use of a cushion of air to support the tube 10 prevents surface deformation, including scratches, from occurring at a time when the tube 10 is wet and easily damaged.

#### THE DRYER 16

Referring to FIG. 5, the dryer 16 includes a hollow, cylindrical shell 90. Insulation 92 is disposed about the shell 90. A pair of end plates 94, 96 support the shell 90. The plate 94 is rigidly secured to the shell 90, while the plate 96 is loosely connected to the shell 90 in order to accommodate expansion.

A pair of O-ring-fitted brass plugs 98 are disposed at each end of the shell 90. The plugs 98 are supported concentrically relative to the shell 90 by means of supports 100. The plugs 98 and the supports 100 enclose the ends of the shell 90, thereby creating a chamber 102.

A porous graphite tube 104 is disposed within the chamber 102 and is supported by means of the plugs 98. The tube 104 includes a plurality of radially extending openings 106 that are spaced along the length of the tube 104. A conduit 108 extends through the shell 90 and is connected thereto by means of a fitting 109. The conduit 108 enables hot air from a source (not shown) to be directed into the chamber 102.

The clearance between the outer diameter of the newly extruded tube 10 and the inner diameter of the tube 104 is rather small. For example, if the newly extruded tube 10 has a nominal outside diameter of 0.615 inch, the tube 104 typically will have a nominal inside diameter of 0.75 inch. In order to insure proper airflow, the openings 106 have a diameter of about 0.040 inch, and are spaced 4 holes about every twelve inches along the length of the tube 104 in a 360° pattern. The conduit 108 enters the chamber 102 at an axial location about 62% of the length of the chamber 102. Accordingly, hot air directed into the chamber 102 will tend to warm the exit end of the chamber 102 more than the entrance end.

As will be apparent from an examination of FIG. 5, heated air directed into the chamber 102 will pass through the openings 106 and closely surround the tube 10. Heated air will be discharged from the dryer 16 at each end of the tube 104. The heated air that enters the tube 104 tends to support the tube 10 on a cushion of air, in a manner similar to the tube guide 14.

#### THE FIRST PINCH ROLLS 18

Referring to FIGS. 6-8, the first pinch rolls 18 include an upper roll 110 and a lower roll 112. The rolls 110, 112 each have a soft rubber coating 114 on their outer surface. The coating 114 has a 70 durometer hardness rating. The roll 110 includes a circumferential groove 113 that is adapted to conform generally to the outer diameter of the tube 10. The lower roll 112 includes a circumferential groove 115 that also is adapted to conform to the outer diameter of the tube 10.

A shaft 116 supports the roll 110 for rotation. An air cylinder 118 is connected to the shaft 116 by means of a

rod 120. The lower roll 112 is supported for rotation by means of a drive shaft 122 projecting from a DC gearmotor 124. The gearmotor 124 is equipped with a tachometer speed control and can maintain very precise adjustable speeds. If desired, the tachometer speed control could be connected to the extruder 12 to automatically correlate the speed of extrusion with the pinch roll speed.

As will be apparent from an examination of FIGS. 6-8, the lower roll 112 is fixed relative to the horizontal. The air cylinder 118 can be activated to space the roll 110 a large distance from the roll 112 for purposes of threading the tube 10 initially. Thereafter, the cylinder 118 is activated to close the roll 110 against the tube 10 and to compress the tube 10 against the lower roll 112. The air cylinder 118 includes an adjustable air supply to permit the pressure on the tube 10 to be maintained at a desired low pressure. The lower roll 112 is driven by the gearmotor 124 at a desired low speed to apply a slight tension to the tube 10.

#### THE CALCINER 20

Referring to FIGS. 9 and 9A, the calciner 20 includes a cylindrical shell 130, a liner 132 concentrically disposed within the shell 130, and insulation 134 disposed intermediate the shell 130 and the liner 132. A pair of end plates 136, 138 close the ends of the calciner 20.

An elongate, cylindrical, stainless steel tube 140 is concentrically disposed within the liner 132. The tube 140 is maintained in place within the liner 132 by means of radially extending supports 142. A plurality of electrical heating elements 144 are disposed about the liner 132. Spaced conduits 146 open through the shell 130 along its bottom, and are connected to the shell 130 by means of fittings 148. Lead lines 150 extend through the conduit 146 and into the interior of the shell 130 in order to provide electrical current to the heaters 144.

As illustrated, two separate sets of heating elements 144 are provided. The temperature of the calciner 20 is variable and is controlled by a temperature controller and thermocouple (not shown). A fume hood (not shown) is positioned adjacent the end plate 136 at that point where the tube 10 enters the calciner 20. The fume hood withdraws gases from the interior of the calciner 20 for disposition elsewhere.

As will be described subsequently, an inert atmosphere is maintained within the calciner 20. It is important that gases flow through the calciner 20 from the exit end toward the entrance end so that no oxygen-bearing gases can enter the sintering furnace 24.

#### THE TRANSITION TUBE 22

The transition tube 22 is shown in FIG. 9 as being connected to the end plate 138. The transition tube 22 is approximately 24 inches long, and has an inner diameter slightly larger than the outer diameter of the tube 10. If, for example, the tube 10 has an outer diameter of 0.625 inch, then the inner diameter of the transition tube 22 should be on the order of 0.6875 inch.

The transition tube 22 is not heated. Accordingly, the tube 10 becomes cooled during its passage through the transition tube 22. The transition tube 22 isolates the oxygen-bearing gases released during calcining from the much hotter sintering furnace 24.

#### THE SINTERING FURNACE 24

Referring to FIGS. 10-12, the sintering furnace 24 includes a large, cylindrical shell 160 having radially

extending flanges 162 at each end. A graphite box 164 having a rectangular cross-section (FIG. 12) is disposed centrally within the shell 160. The box 164 includes a top plate 166, a bottom plate 168, side plates 170, a tube guide 172, and tube guide supports 174.

The box 164 encloses a plurality of graphite resistor heating elements 176. The heating elements 176 are disposed on either side of the tube guide 172 along the length of the tube guide 172. The heating elements 176 are connected at their upper ends by means of graphite connectors 178, which in turn are connected to graphite power rods 180. The power rods 180 are connected to a source of electrical current (not shown) that energizes the heating elements 176. A pair of optical pyrometer sight ports 181 extend through openings formed in the shell 160 and the box 164 in order for the internal temperature of the box 164 to be monitored and for inert gas to be directed into the box 164.

A pair of insulated end caps 182 are provided for the box 164 so as to close the ends thereof. The end caps 182 are supported within the shell 160 by an insulated support member 184. The ends of the shell 160 are closed by insulation barriers 186 that engage the ends of the end caps 182 and the support members 184. The end caps 182 and the insulation barriers 186 include small, longitudinally extending openings 187 that permit the tube 10 to enter and leave the sintering furnace 24. The insulated end caps 182, the support members 184, and the barriers 186 are made of graphite foam or similar material.

The interior of the shell 160 is filled with high purity acetylene black having a density of about 9 lb/ft<sup>3</sup>. The acetylene black is indicated by the reference numeral 188. Insulation barriers 190 are provided for the power rods 180 and the sight ports 181 where they extend from the upper plate 166 through to openings formed in the upper surface of the shell 160.

Referring particularly to FIG. 11, the tube guide 172 is an elongate, "fine grain" graphite member having a large diameter section 192, a small diameter section 194, and a tapered transition area 196. The transition area 196 is in the form of a beveled shoulder that is located at approximately the center of the sintering furnace 24. The centerline of the tube guide 172 is aligned with the centerline of the tube 10 being moved through the sintering furnace 24.

The tube 10 shrinks upon being sintered. The linear shrinkage is approximately 18% for the preferred alpha silicon carbide ceramic powder described previously. By aligning the longitudinal axis of the tube guide 172 with that of the tube 10, and by constricting the inner diameter of the tube guide 172 as described previously, the tube 10 will be adequately supported at all times during its passage through the sintering furnace 24. A controlled small clearance of about 0.060 inch on the diameter is maintained between the tube guide 172 and the tube 10. Because the tube 10 is well supported and because its longitudinal centerline is kept straight during sintering, the straightness of the finished tube 10 is greatly enhanced.

#### THE COOLER 26

Referring to FIGS. 13 and 14, the cooler 26 includes a cylindrical shell 200 within which a second, smaller, cylindrical shell 202 is concentrically disposed. A small chamber 203 is formed between the shells 200, 202. End plates 204, 206 close the shells 200, 202 and define the ends of the chamber 203. End caps 207 are carried by

the plates 204, 206 and support a longitudinally extending graphite tube guide 208 concentrically within the shell 202. The end caps 207 are made of a strong insulating material such as graphite foam.

A conduit 209 is connected to the shell 200 and includes a fitting 210 that is adapted to be connected to a source of cooling fluid such as water. A second conduit 212 is connected to the shell 200 and also includes a fitting 214 for connection to a fluid discharge (not shown). The inner diameter of the second shell 202 is relatively large, creating an elongate, large-diameter chamber 216 through which the tube guide 208 extends.

A vertically extending sleeve 218 is concentrically disposed within the conduit 209. Similarly, a vertically extending sleeve 220 is concentrically disposed within the conduit 212. The sleeves 218, 220 open into the chamber 216. The gap between the upper ends of the conduits 209, 212 and the sleeves 218, 220 is closed by flanged rings 222. The flanged rings 222 seal off the openings defined by the sleeves 218, 220.

As will be apparent from an examination of FIG. 13, cooling fluid that is directed into the conduit 209 fills the chamber 203 and is discharged through the conduit 212. The shell 202 will be chilled and, in turn, the heated tube 10 passing through the tube guide 208 will be cooled, primarily by radiation.

#### THE EXIT TUBE GUIDE 28

The exit tube guide 28 is located downstream of the end plate 206. The exit tube guide 28 can be substantially similar to the adjustment mechanism for the die 48 included as part of the extruder 12. The exit tube guide 28 is closely fitted to the tube 10 (about 0.063 inch clearance). The exit tube guide 28 can be adjusted radially relative to the centerline of the tube 10 in order to produce small deflective forces on the tube 10. The exit tube guide 28 is adjusted in a trial and error manner to produce tubes 10 having maximum straightness. The use of the exit tube guide 28 in conjunction with the tube guide 172 included as part of the sintering furnace 24 produces excellent straightness characteristics in the finished tube 10.

A horizontally extending sleeve 224 (FIG. 15) projects downstream from the exit tube guide 28. The end of the sleeve 224 is closed by a rubber boot seal 226 that has a small opening at its center through which the tube 10 passes in closely fitting relationship. Inert gas such as argon or nitrogen is introduced into the exit tube guide 28 under pressure and flows upstream through the cooler 26. The gas is discharged from the calciner 20 into the fume hood located adjacent the end plate 136. The inert gas thus surrounds the tube 10 while it is being treated at elevated temperatures.

#### THE SECOND PINCH ROLLS 30

Referring to FIGS. 15 and 16, the second pinch rolls 30 include a first roll 230 and a second roll 232. The first roll 230 is supported for rotation about a vertical axis by means of a drive shaft 234. The roll 230 is prevented from rotating relative to the drive shaft 234 by means of a key 235. The shaft 234 is supported for rotation by bearings 236, which in turn are supported by brackets 237. The shaft 234 is driven by a magnetic particle clutch 238. The clutch 238 is driven by a gear reducer 240, which in turn is driven by a D.C. gearmotor 242. The gear reducer 240 is supported by a bracket 241, while the gearmotor 242 is supported by a bracket 243.

The gearmotor 242 and the gear reducer 240 are connected by a coupling 244. The gear reducer 240 and the clutch 238 are connected by a coupling 246. The clutch 238 is connected to the drive shaft 234 by means of a splined connection indicated at 248.

The roll 232 is supported for rotation by bearings (not shown) which in turn are supported by a shaft 250. The shaft 250 is supported by upper and lower bearings 252, which in turn are supported by support brackets 254 having a laterally extending slot 255. The bearings 252 are engaged by upper and lower actuating rods 256. The other ends of the rods 256 are connected by a header plate 260, which in turn is connected to an air cylinder 262.

A frame 264 supports the brackets 237, 241. An opposing frame 266 supports the bracket 243 and the rods 256. Referring to FIG. 15, pinch roll support brackets 268 provide support for a laterally extending adjustment rod 270. The rod 270 is secured at one end to the frame 264 and extends through the header plate 260 at its other end. An adjustment knob 272 is provided for the rod 270.

As will be apparent from an examination of FIGS. 15 and 16, the first roll 230 is driven, while the second roll 232 is not. The first roll 230 is stationary relative to the frames 264, 266, while the second roll 232 can move laterally relative thereto (and relative to the tube 10). The adjustment rod 270 moves the driven roll 230 and thus the whole framework laterally relative to the centerline of the sintered tube 10, thus allowing the driven roll 230 to be positioned as desired for various tube diameters.

The rotation of the rolls 230, 232 is carefully controlled relative to the first pinch rolls 18 by means of a voltage adjustment of the clutch 238. The rolls 230, 232 are operated such that a constant tension of approximately 6-7 pounds is applied to the tube 10 at any given line speed. This amount of constant tension has been found to be a considerable aid to tube straightness, as well as a means by which friction through the line can be overcome.

#### THE CUT-OFF MECHANISM 32

Referring to FIGS. 17, 18 and 19, the cut-off mechanism 32 includes a rectangular frame, or carriage 280. The carriage 280 includes a pair of spaced, box-like, laterally extending frame members 282 that are connected by a pair of spaced, axially extending frame members 284. The frame members 282, 284 are welded together with the aid of gussets 285 to form a rigid structure. The carriage 280 is mounted for movement along tubular rails 286. The rails 286 are aligned with the direction of travel of the tube 10. The carriage 280 is mounted to the rails 286 by means of low-friction ball bearings 288 that are included as part of the frame members 282. A weak spring (not shown) biases the carriage 280 to the right as viewed in FIG. 17.

A pair of clamps 290 are provided to grip the tube 10 during its passage through the cut-off mechanism 32. Referring particularly to FIG. 18, each clamp 290 includes a lower tube support 292, an upper tube support 294, an air cylinder 296, and a rod 298 projecting from the cylinder 296 to which the upper tube support 294 is attached. The cylinders 296 are connected to the frame members 282 by means of brackets 300.

A diamond cut-off wheel 302 is disposed beneath the tube 10. The wheel 302 is supported for rotation about an axis parallel to the longitudinal axis of the tube 10 by

means of a shaft 304. The shaft 304 is supported for rotation by bearings 306 that are mounted to a housing 308. The housing 308 includes a guard 310 that has a slot 312 through which the wheel 302 extends. The shaft 304 is provided with a drive pulley 314 about which a drive belt 316 is reeved. A drive motor (not shown) is connected to the outside of the housing 308. The drive belt 316 passes through a slot 318 formed in the lower portion of the housing 308 for connection to the drive motor.

A variable speed DC gearmotor 320 is provided to drive the housing 308 (and with it the motor and the wheel 302) up and down. The motor 320 is supported by a mounting bracket 322. A ball screw 324 is connected to the motor 320. The ball screw 324 passes through a bracket 326 that is connected to the housing 308. A plurality of vertically extending guide tubes 328 (FIGS. 17 and 19) are connected to the housing 308 by means of brackets 330. The tubes 328 mate with guide brackets 332 that are securely attached to the frame members 282.

As will be apparent from the foregoing description, whenever it is desired to cut the tube 10, the clamps 290 are actuated so that the tube 10 is gripped. Due to the extremely low friction in the bearings 288 and due to the weakness of the retaining spring, the carriage 280 will begin to move to the left as viewed in FIG. 17. The force required to drive the carriage 280 is approximately 1.0-2.0 pounds. Although this force temporarily detracts from the force being applied to the tube 10 by the second pinch rolls 30, the temporary change in tension applied to the tube 10 has not been found to be detrimental.

As the carriage 280 is being moved due to the axial force supplied by the tube 10, the cut-off wheel motor is activated and the gearmotor 320 is energized so as to drive the housing 308 upwardly at a very slow variable rate (about 45 seconds for the complete upward excursion). The tube 10 is severed by the wheel 302 during the upward excursion of the housing 308. It takes about 15 seconds for the tube 10 to be severed. After the tube 10 has been severed, the motor 320 retracts the housing 308 quickly, and the clamps 290 are released to free the now-severed ends of the tube 10. The carriage 280 is returned to its rest position under the influence of the return spring.

#### THE INSPECTION TABLE 34

Referring to FIG. 20, the inspection table 34 includes a plurality of horizontally disposed rollers 340. A first, elongate hose 342 is wrapped about a reel 344. As illustrated, the hose 342 extends across the rollers 340 and is connected to the end of the tube 10 by means of a clamp (not shown). A second hose 346 also is provided and is wrapped about a separate reel (not shown). The hoses 342, 346 enable inert gas such as argon or nitrogen to be supplied under pressure into the interior of the tube 10. The source for the gas is not shown.

The hoses 342, 346 are wrapped about idler pulleys 348, 350, respectively. A variable speed motor 352 includes a drive shaft 354 that is in contact with the hoses 342, 346 that are passed over the pulleys 348, 350. The hose reels are spring-loaded so that they always tend to retract the hoses 342, 346. The motor 352 and its drive shaft 354 control the rotation of the pulleys 348, 350 so as to match the retraction speed of the hoses 342, 346 with the speed of the tube 10 exiting the cut-off mechanism 32. Desirably, the hoses 342, 346 are retracted at a

speed equal to the speed of the tube 10 without applying spring tension from the hose reels to the tube 10. The hoses 342, 346 thus apply little or no axial force to the tube 10.

The inspection table 34 can be as long as desired, limited only by space constraints or by the desire to manufacture tubes 10 having a certain fixed length. For example, the table 34 could extend to substantial lengths such as 60 feet or more. For most purposes, however, the table 34 can be approximately 20 feet in length.

As will be apparent from an examination of FIG. 20, the hose 342 will be retracted as the tube 10 being extruded passes through the cut-off mechanism 32. After the tube 10 has been severed, the second hose 346 can be extended and connected to the newly severed tube 10. It is expected that the flow of inert gas passing through the tube 10 will be stopped only a minute or two as the hose 346 is being connected. The connection should be made as quickly as possible in order to minimize the time when inert gas is not passing through the tube 10.

After the tube 10 has been fully extended across the table 34 and is being supported by the rollers 340, the hose 342 is disconnected. The tube 10 then is ready for testing. The table 34 includes a horizontally extending floor 356 from which a short, vertically extending wall 358 projects at right angles. The floor 356 and the wall 358 are carefully positioned relative to each other so that an accurate straight edge is provided. The tube is placed on the floor 356 and is pressed against the wall 358. Any deviations from a straight line can be measured easily. The tube 10 generally will be considered acceptable for most commercial purposes if the deviation from a straight line is equivalent to one inch of lateral deflection for a 20-foot long tube.

After the straightness of the tube 10 has been determined, the tube 10 is ready for pressure testing. A trough 360 is disposed adjacent the floor 356. The trough 360 is generally U-shaped in cross-section. A hose 362 that is connected to a check valve is disposed at one end of the trough 360. A pump 364 is disposed adjacent the other end of the tube 10 and is connected to the tube 10 by means of a hose 366. After the tube 10 has been filled with water, it is pressurized by the pump 364 to a pressure whose value depends upon the desired tensile hoop stress to be applied to the tube, the tube outer diameter, and the tube wall thickness. For sintered alpha silicon carbide tubes 0.5 inch in diameter with a wall thickness of 0.060 inch, a pressure test of approximately 2600 p.s.i.g. is adequate. The pressure is maintained for approximately 30 seconds. The test pressure exceeds any pressure likely to be encountered in use by at least 50 percent. If the tube 10 sustains the test pressure for the period indicated, then the tube 10 is ready for packaging and shipment to the customer.

### OPERATION

Although the overall operation of the tube-making apparatus according to the invention will be apparent from the foregoing description, certain guidelines should be followed in operating the apparatus. Generally speaking, the smaller the diameter of the tubes 10, and the thinner the side walls of the tubes 10, then the faster the line can be operated. Conversely, larger tubes and/or thicker-walled tubes will require longer processing times. To produce a tube having a finished nominal outside diameter of 0.500 inch, and a side wall thickness of 0.060 inch, the following conditions apply:

1. Extrusion of the tube 10 should be on the order of 4.9 inches per minute. It is expected that extrusion rates of up to about 12 inches per minute can be attained, if desired. The nominal outside diameter of the tube 10 is about 0.615 inch when newly extruded.

2. A tapered graphite threading plug is inserted into the forward end of the tube 10 to assist in guiding the tube 10 through the line. Each of the elements described previously such as the calciner 20 includes a conical entrance guide (not shown) in order to assist in initially threading the tube 10 through the tube-making apparatus.

3. In order to provide a proper cushion of air in the tube guide 14, the openings in the porous plugs 84 must be sized correctly. If the openings are too large, too much flow would be required for proper performance. If the openings are too small, portions of the tube 10 will not be supported or else holes in the tube wall will be created. The plugs 84 should have openings with diameters on the order of 5 microns for best performance.

4. As illustrated, the dryer 16 is approximately 103 inches long. The air supply temperature is approximately 175° C. at a pressure of about 5-10 p.s.i.g. The flow rate of the heated air is about 500 s.c.f.h. As shown in FIG. 22, the inlet temperature of the dryer 16 is about 80° C. The temperature climbs smoothly to an exit temperature of about 175° C.

If the temperature in the dryer 16 is too high, the tube 10 will be blistered. If the temperature is too low, the tube 10 will not be dried, and it will be damaged by the pinch rolls 18. The length of the dryer 16 is a function of the desired line speed and the wall thickness of the tube 10. If the flow rate of the drying gas is too high, it can create holes in the tube wall. If the flow rate is too low, the tube 10 will not float on a cushion of air but rather will drag.

5. The first pinch rolls 18 apply a very low axial tension to the tube 10. It has been found that the first pinch rolls 18 should have a surface speed of about 2% faster than the speed of the tube 10 as it emerges from the dryer 16 to prevent buckling of the newly extruded tube 10. The speed of the pinch rolls 18 must be controlled carefully, however, because the tube 10 will break at approximately 6% overspeed. If the pinch rolls 18 are controlled properly, they can be used to slightly adjust the diameter of the tube 10.

6. The calciner 20 is approximately 84 inches long. The heating elements 144 cause the liner temperature in the center of the downstream hot zone to be about 600° C. At this temperature, the organic material in the tube 10 decomposes and is vaporized. Approximately 1 foot inside the calciner 20 the temperature reaches about 200°-225° C. The temperature gradient inside the calciner 20 (see FIG. 22) prevents oxidation of the tube 10 by increasing the distance between the hot zone and the room atmosphere at the entrance to the calciner 20. The temperature gradient also is relatively gradual to avoid blistering the tube 10.

If the calcining temperature is too hot, the tube 10 will be subjected to accelerated oxidation in the calciner, causing poor final quality. If the calcining temperature is too low, incomplete calcining will occur. As with the dryer 16, the length of the calciner 20 is related to the tube wall thickness and the line speed.

7. As the tube 10 enters the sintering furnace 24, the temperature rises rapidly from about 400° C. to the maximum temperature of about 2250°-2300° C. within about 12 inches of tube travel. The maximum tempera-



ture is selected as a function of the composition of the tube 10 being sintered and the inert gas that is used. Argon permits lower temperatures, while nitrogen requires higher temperatures (with silicon carbide tubes). It is preferable to sinter the tube 10 at a lower temperature for a longer period of time in order to prevent excessive grain growth of the tube 10.

Periodically, about every 2-4 weeks, the furnace 24 is charged with powdered boron carbide on the bottom of the box 164. A boron-containing gas is formed at sintering temperature that surrounds the tube 10 and aids sintering.

At a line speed of 4.9 inches per minute, maximum temperature is attained within less than three minutes. As the tube 10 attains maximum temperature, it becomes sintered. The tube 10 shrinks in length approximately 18 percent. The tube guide 172 maintains proper contact with the tube 10 and assures tubes straightness during the sintering process.

It is important that the tube 10 stay at maximum temperature long enough to ensure proper sintering action. The minimum time believed to be adequate for attaining adequate sintering action is about 6-10 minutes. In order to attain adequate residence time in the sintering furnace 24 at the line speed selected, the heating zone in the sintering furnace 24 is about 50 inches long.

The oxygen level in the sintering furnace 24 is maintained at about 7-15 parts per million during operation. The approximate furnace steady-state power consumption is about 20 kw, and heat-up time is about two hours after an inert gas pre-purge cycle. The heating elements 176 are operated at about 55 volts AC maximum.

If necessary or desired, the tube 10 can be maintained at maximum temperature for about 2 hours without damage. If damage occurs, it will be in the nature of undesired grain growth. The fact that the tube 10 can be maintained at maximum temperature for a long period of time means that the line can be slowed down if necessary to very low speeds on the order of 0.5 inch per minute or even 0.25 inch per minute.

At the entrance to the sintering furnace 24, a slow condensation build-up of silicon plus  $\text{SiO}_2$  will occur from the silicon-bearing gas species generated within the furnace 24. This condensation is believed to occur as the gas cools upon leaving the furnace 24 and requires occasional removal (about every week or two) from the bore surrounding the tube 10.

It has been found that the tube guide 172 experiences no appreciable wear. This is believed to be a result of low friction imparted by the tube 10, as well as a result of wear-resistant deposits that form on the inner diameter of the tube guide 172.

As the tube 10 exits the sintering furnace 24, it will be traveling at a lower rate of speed due to shrinkage. The exit speed typically is about 4 inches per minute. As the tube 10 passes through the cooler 28, it is cooled rapidly to approximately 40° C. This rapid chilling of the tube 10 has not been found to be harmful to the tube 10.

8. As the tube 10 passes through the exit tube guide 28, the tube guide 28 is adjusted as described previously to straighten the tube as much as possible. It has been found that tube straightness is governed primarily by the geometry of the sintering furnace tube guide 172, the adjustment of the exit tube guide 28, and the tension applied by the second pinch rolls 30. The exit tube guide 28 should be relatively far from the end of the sintering furnace 24 (about 5 feet) in order to ensure a long moment arm for bending the tube 10 as may be necessary.

9. During the cut-off operation, the vacuum blower 76 is deactivated to avoid drawing air into the tube 10. As the tube 10 passes the cut-off mechanism 32, one of the hoses 342, 346 is connected to the end of the tube 10. Inert gas is pumped under pressure into the tube 10. Simultaneously, the vacuum blower 76 is activated in order to draw the inert gas and volatiles produced by the tube 10 through the interior of the tube 10, through the mandrel 60, and out of the extruder 12 for disposition. The reading on the vacuum gauge 70 should be maintained at approximately 8-15 inches of water. The flow rate as measured by the flowmeter 74 should be approximately 20-40 s.c.f.h. It has been found that the blower 76 needs to have a rating of at least 50 inches of water in order to overcome all pressure drops throughout the system.

The throttle valve 78 occasionally is adjusted to maintain desired readings as the trap 72 accumulates liquids and solids. Dilution air is added as needed to cool the blower 76 and to permit control of the desired vacuum level. It has been found that too high a vacuum level, for example 35 inches of water (for a 0.060 sintered wall thickness), can collapse the tube 10 immediately downstream of the extruder 12.

A fully charged extruder 12 can produce approximately 140 lineal feet of finished tube having the dimensions previously described. Approximately 20 feet of finished ceramic tube can be produced each hour. It has been found that about 3 pounds of extrudable mixture will yield about 20 feet of finished ceramic tube of these dimensions. A certain portion of the tube 10 must be scrapped due to a lack of internal inert gas being available. Nevertheless, even taking into account scrap that occurs at the head and tail ends of a long run, very good yields on the order of 90% or more of high quality ceramic tube can be produced.

The invention as illustrated shows only a single tube 10 being produced, but it is expected that a number of small tubes 10 may be produced in multiple simultaneous strands, provided that relatively large spaces, for example 5 diameters or more, are left between individual strands.

The tube-making apparatus is equipped with suitable automatic controls, such controls being known to those skilled in the art and not requiring further description here other than the description that has been provided already. Upon loading a new billet into the extruder 12, it is expected that the newly loaded billet will "weld" itself to the previous billet within the bore 38. Reloading of a new ceramic billet will require stopping the extrusion of the tube 10 for only a minute or two and should not affect the quality of the tubes 10 being extruded.

If it is desired to manufacture tubes from oxide ceramics instead of the preferred alpha silicon carbide, then two options are possible: (1) the equipment may remain as previously described and the operating parameters, chiefly the sintering furnace temperature, may be adjusted as appropriate for the material being processed, or (2) the sintering furnace 24 could be replaced by a conventional, relatively long tube furnace having either  $\text{MOSi}_2$  heating elements for use up to about 1700° C., or silicon carbide heating elements for use up to about 1500° C. and oxide-ceramic fiber insulation. The second option would permit air to be used both inside and outside the tube and could lead to a simpler and lower cost variant of the invention for oxide-ceramic tubes that can be sintered below about

1700° C. These materials would include zirconia, alumina, or mullite. If the second option is selected, a furnace liner tube suitable for operation in air up to about 1600° C. could be used; a suitable material would be sintered silicon carbide.

The tube-making apparatus according to the invention enables extremely long ceramic tubes to be produced on a more or less continuous basis. The tubes can have a wide variety of cross-sectional shapes and wall thicknesses. The tubes can be manufactured extremely straight, with excellent control over symmetry and wall thickness. The present invention minimizes or eliminates damage from frequent tube handling, improves processing symmetry, permits rapid feedback as part of the manufacturing process, and avoids the high capital cost of conventional tube-manufacturing equipment.

Although the invention has been described in its preferred form with a certain degree of particularity, it will be apparent that various changes and modifications can be made without departing from the true spirit and scope of the invention as hereinafter claimed. It is expected that the patent will cover all such changes and modifications. It also is intended that the patent shall cover, by suitable expression in the appended claims, whatever features of patentable novelty exist in the invention disclosed.

What is claimed is:

1. A method of manufacturing ceramic tubes on a substantially continuous basis from a mixture including ceramic powder and organic material, comprising the steps of:

providing a die having a desired cross-section; extruding the mixture through the die to form a tube; supporting the tube after it has been extruded; drying the tube while continuing to extrude the mixture;

supporting the tube while it is being dried; calcining the tube at about 550°-600° C. to decompose the organic material while continuing the extrude the mixture;

supporting the tube while it is being calcined; sintering the tube while continuing to extrude the mixture;

supporting the tube while it is being sintered; cooling the tube while continuing to extrude the mixture;

supporting the tube while it is being cooled; and cutting the tube to length while continuing to extrude the mixture.

2. The method of claim 1, further comprising the step of applying a vacuum to the mixture prior to extruding the mixture through the die.

3. The method of claim 1, further comprising the step of directing the extruded tube along a horizontal path of travel.

4. The method of claim 3, wherein the step of supporting the tube after it has been extruded is accomplished by floating the tube on a cushion of air.

5. The method of claim 1, further comprising the step of applying tension to the tube.

6. The method of claim 5, wherein the step of applying tension to the tube is accomplished by providing first pinch rolls and engaging the tube with the first pinch rolls subsequent to the step of drying.

7. The method of claim 6, wherein the surface speed of the first pinch rolls is about 2 percent greater than the speed at which the tube exits the dryer.

8. The method of claim 6, further comprising the steps of providing second pinch rolls and engaging the tube with the second pinch rolls subsequent to the step of cooling, the second pinch rolls being operated such that tension is applied through the tube upstream to the first pinch rolls.

9. The method of claim 8, wherein the second pinch rolls apply an axial force of about 6 pounds to the tube.

10. The method of claim 1, further comprising the step of maintaining an inert atmosphere around the tube during the steps of drying, calcining, and sintering.

11. The method of claim 1, further comprising the step of maintaining an inert atmosphere within the tube during the steps of drying, calcining, and sintering.

12. The method of claim 11, wherein the step of maintaining an inert atmosphere is accomplished by introducing a controlled flow of inert gas into the open end of the tube downstream of the cooling zone, flowing the inert gas in a direction opposite to the direction of travel of the tube, and removing the inert gas from the tube through the die.

13. The method of claim 1, wherein the step of supporting the tube while it is being dried includes floating the tube on a cushion of heated air.

14. The method of claim 1, wherein the step of calcining is accomplished by providing an open-ended cylindrical member, heating the cylindrical member, and passing the tube through the cylindrical member.

15. The method of claim 14, wherein the cylindrical member is heated to about 550°-600° C.

16. The method of claim 1, wherein the step of supporting the tube while it is being sintered includes the steps of providing a cylindrical tube guide that is sized to accommodate tube shrinkage during sintering, heating the tube guide, and passing the tube through the tube guide.

17. The method of claim 16, wherein the tube guide is heated to about 2250°-2300° C.

18. The method of claim 1, wherein the step of cooling is accomplished by providing an open-ended, water-cooled shell and passing the tube through the shell.

19. The method of claim 1, wherein the step of cutting is accomplished by providing a clamp adjacent the tube, gripping the tube with the clamp, moving the clamp together with the tube in the direction of travel of the tube, and severing the tube while the clamp is gripping the tube.

20. The method of claim 1, further comprising the step of lowering the temperature of the tube between the steps of calcining and sintering.

21. The method of claim 1, wherein the mixture includes silicon carbide, a boron source, a carbon source, a plasticizer, and a solvent.

22. The method of claim 21, wherein the silicon carbide is alpha silicon carbide, the boron source is boron carbide, the carbon source is phenolic resin, the plasticizer is methylcellulose ether, and the solvent is water.

23. A method for manufacturing ceramic tubes from a mixture including ceramic powder and organic material, comprising the steps of:

providing a die having a desired cross-section;

applying a vacuum to the mixture;

extruding the mixture through the die to form a tube;

supporting the tube while continuing to extrude the mixture;

drying the tube at about 175° C. while continuing the extrude the mixture;

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calcining the tube at about 550°-600° C. to decompose the organic material while continuing to extrude the mixture;  
 sintering the tube at about 2250°-2300° C. while continuing to extrude the mixture;  
 cooling the tube while continuing to extrude the mixture;  
 cutting the tube to length while continuing to extrude the mixture;  
 applying tension to the tube while continuing to extrude the mixture, the step of applying tension being accomplished by providing first pinch rolls and engaging the tube with the first pinch rolls subsequent to the step of drying, providing second pinch rolls and engaging the tube with the second pinch rolls subsequent to the step of cooling, the second pinch rolls being operated such that tension is applied through the tube upstream to the first pinch rolls;  
 maintaining an inert atmosphere around the tube during the steps of calcining and sintering; and maintaining an inert atmosphere within the tube during the steps of calcining and sintering.

24. The method of claim 23, wherein the step of supporting is accomplished by floating the tube on a cushion of air.

25. The method of claim 23, wherein the step of maintaining an inert atmosphere within the tube is accomplished by introducing a controlled flow of inert gas into the open end of the tube downstream of the cooling zone, flowing the inert gas in a direction opposite to the direction of travel of the tube, and removing the inert gas from the tube through the die.

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26. The method of claim 23, wherein the step of drying includes floating the tube on a cushion of heated air.

27. The method of claim 23, wherein the step of calcining is accomplished by providing an open-ended cylindrical member, heating the cylindrical member, and passing the tube through the cylindrical member.

28. The method of claim 23, wherein the step of sintering is accomplished by providing a cylindrical tube guide that is sized to accommodate tube shrinkage during sintering, heating the tube guide, and passing the tube through the tube guide.

29. The method of claim 23, wherein the step of cooling is accomplished by providing an open-ended, water-cooled shell and passing the tube through the shell.

30. The method of claim 23, wherein the step of cutting is accomplished by providing a clamp adjacent the tube, gripping the tube with the clamp, moving the clamp together with the tube in the direction of travel of the tube, and severing the tube while the clamp is gripping the tube.

31. The method of claim 23, wherein the mixture includes silicon carbide, a boron source, a carbon source, a plasticizer, and a solvent.

32. A method of claim 31, wherein the silicon carbide is alpha silicon carbide, the boron source is boron carbide, the carbon source is phenolic resin, the plasticizer is methylcellulose ether, and the solvent is water.

33. The method of claim 1, further comprising the step of applying deflective forces to the tube after the tube has been sintered.

34. The method of claim 23, further comprising the step of applying deflective forces to the tube after the tube has been sintered.

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